CONVERSION OF CARBON DIOXIDE TO METHANE AND CARBON MONOXIDE USING ALUMINA BASED CATALYSTS

BY

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I dedicated my work to my family.

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"In the name of Allah, The Most Merciful and The Most Gracious"

All praise and thanks to Allah Almighty, the Creator of all worlds who give me the courage to accomplish this work sincerely and successfully. May there be every peace and blessings upon the holy prophet Hazrat Muhammed (PBUH), his family and his companions.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

SEM	Scanning electron microscopy	X_{CO_2}	Conversion of carbon dioxide
TGA	Thermo Gravimetric Analysis	S_{CH_4}	Selectivity of Methane
XRD	X-ray Diffraction	S_{CO}	Selectivity of carbon monoxide
EDXS	Energy-dispersive X-Ray spectroscopy	RWGS reaction	Reverse water gas shift reaction
GHG	Greenhouse gaes	FT reaction	Fisher-Tropsch reaction
BET analysis	Brunauer–Emmett–Teller analysis	FTIR	Fourier Transform Infrared Spectroscopy

ABSTRACT

Full Name : Waqar Ahmad

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The anticipated worsening of environmental situation due to accumulation of greenhouse gases (GHG) in the atmosphere poses a serious threat to all the circles of life on the earth. Various types of methods including physical and chemical have been practiced industrially to control the emission of CO_2. These technologies require additional expenses to dispose-off the chemical sludge or waste after treatment process. This problem diverted the attention of the scientist towards conversion of voluminous amount of carbon dioxide into valuable hydrocarbons and chemicals by utilization of different metallic and non-metallic catalysts.

This research was conducted to synthesize a metallic catalyst over Al_2O_3 support for methanation of carbon dioxide. For this purpose, impregnation technique was used to prepare different Copper, Potassium and Magnesium catalysts over alumina support. The synthesized catalyst was characterized by XRD, SEM, EDXS, BET, FTIR and TGA to evaluate the phase detection, particle diameter, surface morphology, porosity, percentage loading of metals over a support, pore diameter, BET surface area, presence of functional group, activity and stability of catalyst.

XRD analysis showed the phase of Cu, K and alumina. The SEM images showed aggregated and agglomerated particles over the surface of catalyst, where a homogeneous

distribution of copper and potassium compounds over alumina. Percentages of copper and potassium over alumina support were also confirmed by EDXS. BET analysis showed that catalyst was mesoporous and BET surface area of synthesized catalyst was 114.98 m^2/g.

The research results also include the effect of operational parameters on the conversion of CO_2 to methane. Effect of Cu loading, temperature and molar feed ratio were investigated for synthesized catalysts against carbon dioxide conversion and methane selectivity. For temperature effects, CO_2 conversion and CH_4 selectivity was calculated at different temperatures for prepared catalysts. Similarly, conversion of carbon dioxide and selectivity of methane was noticed at different feed ratios of H_2/CO_2 to check the effect of molar feed ratio of H_2/CO_2.

ملخص الرسالة

الاسم الكامل: وقار احمد

عنوان الرسالة: تحويل ثاني اكسيد الكربون الى ميثان واحادي اكسيد الكربون باستعمال حفاز متأسس من الالومينا

التخصص: هندسة الكيميائية

تاريخ الدرجة العلمية: مايو 2015

التدهور المتوقع للبيئة بسبب تكتل غازات الاحتباس الحراري (GHG) في الغلاف الجوي تمتلك مخاطر عديدة على الدورات الحيوية على الارض. توجد عديد من الطرق الفيزيائية والكيميائية المتبعة في الصناعة للتحكم في انبعاث ثاني اكسيد الكربون. هذه الطرق تتطلب تكلفة اضافية للتخلص من الرواسب الكيميائية او فضلات من عملية التنقية. هذه المشكلة وجهت اهتمام العلماء لتحويل كميات ضخمة من ثاني اكسيد الكربون الى هيدروكربونات وكيماويلت مفيدة بواسطة حفازات معدنية ولامعدنية.

في هذه الاطروحة تم تحضير حفاز معدني على Al_2O_3 لعملية تحويل ثاني اكسيد الكربون الى ميثان. لذلك,تم استعمال تقنية التحميل لتحضير حفازات مختلفة من Mg- K -Cu على الالومينا. الحفاز المحضر قد تم اختباره عن طريقXRD, SEM, EDXS, BET, FTIR, TGA لتحديد الحالة وقطر الجسيمات والتشكيل السطحي والمسامية ونسبة تحميل المعادن وقطر المسام ومساحة السطح ووجود الزمرات الوظيفية ونشاط واستقرار الحفاز.

اوضح تحليل XRD طور كل من Cu وK و الالومينا. صور SEM جسيمات متراكمة ومتكتلة على سطح الحفاز, مع توزيع متجانس من النحاس والبوتاسيوم على الالومينا. تم توكيد نسبة النحاس والبوتاسيوم على الالومينا بـ EDXS. تحليل BET اوضح ان الحفاز متوسط المسامية مساحة السطح 114.98 m^2/g.

نتائج البحث ايضا تضمنت تأثير عوامل التشغيلية على تحويل ثاني اكسيد الكربون الى ميثان. تأثير تحميل النحاس ودرجة الحرارة ونسبة المولية للتغذية قد تم دراسته مع تحويل ثاني اكسيد الكربون وانتقائية الميثان. بالنسبة لتأثير الحرارة, تم حساب تحويل ثاني اكسيد الكربون وانتقائية الميثان في درجات حرارة مختلفة. وبالمثل, تحويل ثاني اكسيد الكربون وانتقائية الميثان مع ونسب مولية مختلفة من H_2/CO_2 للتأكد من تأثير والنسب المولية المختلفة للتغذية.

CHAPTER 1

INTRODUCTION

1.1 Background

Emanation of CO_2 in the atmosphere is increasing day by day which is due to increasing population of the world, grooming of industry and economic development. In the interim, combustion of fossil fuel is another main source for increasing the CO_2 in the atmosphere. Along these lines, overabundance of CO_2 in the atmosphere is a real threat for world climate[1–3]. This excess amount of CO_2 has severe impact in the atmosphere. It is causing global warming and increasing the global temperature, overwhelming rains, storms, ocean acidification and new sorts of diseases[4,5].

Before the industrial revolution, the concentration of CO_2 in atmosphere was 290 ppm however in 2010; it was increased up to 390 ppm. Therefore, at the end of this century, it is anticipated that the concentration of CO_2 in atmosphere will be 570 ppm[3,6]. It is believed that CO_2 emission in Saudi Arabia is increasing at a very fast rate. According to a report, emission rate of CO2 in Saudi Arabia is 16.2 tones per person whereas the emission rate of CO_2 in Middle East, OECD and the world are 7.8, 9.8 and 4.3 tones per person, respectively (IEA, 2011b)[7]. It is also believed that UAE carbon dioxide emission rate has reached at 39 tons CO2/per person/per year which is the second largest emission rate. Especially, Qatar is emitting CO_2 at a rate of 69 tons CO_2/per person/per

year which is largest CO_2 per capita(WRI,2007)[8]. Due to this reason, it is an incredible challenge for countries as well as scientists to overcome or control the emission of CO_2.

In fact, it is an alarming situation for the world because greenhouse gases emissions are increasing in the atmosphere with alarming rates[9]. Therefore, emission of carbon dioxide must be reduced, captured and utilized as a feed stock for other products. It is a very long term and comprehensive project to reduce the emission of CO_2 from different sources. Therefore, for this purpose there are three feasible ways in which its amount can be minimized from the atmosphere. The first strategy for reduction of carbon dioxide is to control the production of CO_2. Second strategy is to store the CO_2. Third strategy is to use the carbon dioxide into a process and produce a valuable product. For the first strategy, it is necessary to shift from the fossil fuel to any other fuel which has less carbon contents especially hydrogen and renewable energy fuel can be used for this purpose. For the second strategy, it is a very challenging task to develop a technology by which it can be separated, captured and stored[6]. Hence, in recent years, a lot of efforts and attention is paid on this topic. In carbon dioxide capture and separation process, CO_2 removal is carried out by the help membrane technology or by using different adsorbents/absorbents[9]. For the third strategy, Scientists are also paying a lot of attention towards this task and converting it into valuable product.

For synthesis of different organic chemicals, materials and carbohydrates; CO_2 is utilized as a C_1 building block because it is very economical, renewable, safe and easily accessible carbon source[10–12]. Carbon dioxide utilization as a feedstock can not only reduce the amount of CO_2 in the atmosphere and change the global climate but for catalytic and industrial growth, it can also present a great challenge for the development

of new processes, concepts and scopes[3,13,14]. Due to thermodynamic stability of CO_2, utilization of CO_2 as a chemical feedstock is very limited. For synthesis of urea and its derivatives, salicylic acid and carbonates, CO_2 is used as a chemical feedstock. In fact, conversion of CO_2 to other chemicals can be accomplished with the help of high energy materials and electro-reductive processes. Conversion of carbon dioxide can be carried out with the help of hydrogen because hydrogen is a very high energy substance. Therefore, hydrogenation of CO_2 can be used for the production of fuels and chemicals[3].

Carbon dioxide is promptly accessible from numerous sources such as byproduct of our industry especially it can be taken from distillery plants, flue gases of the power plants which are using gas, oil or coal. It can also be taken from air or seawater. By combination of reverse water-gas shift reaction and Fisher-Tropsch reaction, CO_2 can be converted into the hydrocarbons. There are a lot of catalytic reactions in which CO_2 is used and converted into valuable products. Therefore, hydrogenation of CO_2 is likewise a good approach to convert CO_2 into methane, methanol, dimethyl ether and other hydrocarbons in the vicinity of a catalyst[1,2].

Hence, hydrogenation of the CO_2 is a promising technique to convert it into hydrocarbons in the presence of catalyst over a support. For this purpose, different catalysts have been produced for conversion of CO_2. These catalysts are Fe, K, Mn, Co, Cu, Zr, Pt, and group VIII metals supported on Al_2O_3, ɣ-Al2O3, SiO_2, Al_2O_3:MgO and Zeolite[1–3,5,8,15–21]. These catalysts and supports define the type of products, product selectivity and conversion on a wide range. Despite that, much effort has been made for the conversion

of carbon dioxide to hydrocarbons but there is still a room for the development of a new catalyst that accounts for the effect of existing multi metals as a surface of support.

1.2 Objectives

The main objective of this project is to synthesize a novel, cost effective, active and stable catalyst which can be used to convert the CO_2 into hydrocarbons by hydrogenation of carbon dioxide.

The specific objectives can be summarized as follows:

- Synthesis of different combinations of Cu, K and Mg catalysts over Al_2O_3.
- Characterization of catalyst.
    - BET surface area
    - XRD analysis
    - TGA analysis
    - SEM analysis
    - EDXS analysis
    - FTIR analysis
- Study the effect of temperature, pressure and molar ratio on conversion of carbon dioxide.
- Study the activity and reproducibility activity of synthesized catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Processes for CO_2 utilization

There are many processes in which CO_2 is utilized as a chemical feedstock and converted into valuable products. Some of these processes have been shown below

- Dry reforming of methane
- Oxidative coupling of methane
- Oxidative dehydrogenation
- Synthesis of urea and urethane derivatives
- Synthesis of carboxylic acid
- Hydrogenation of CO_2

2.1.1 Dry reforming of methane

Dry reforming is a process in which CH_4 is reacted with CO_2 and converted into syngas. During the dry reforming, CO_2 is served as carbon source as well as it is served as oxidant. The reaction for production of syngas through this process is as follow

$$CH_4 + CO_2 \leftrightharpoons 2CO + 2H_2 \quad (1)$$

The nature of this reaction is equilibrium limited and highly endothermic. The syngas which is produced from this reaction has high content of carbon monoxide as compared to steam reforming of methane. So, the ratio of hydrogen to carbon monoxide from this

reaction is almost unity. According to conversion and selectivity point of view, nickel based catalyst and noble metal support has been showed the best performance for this catalytic reaction. But, noble metal is very expensive and rare so development of improved nickel catalyst support is a good approach which can be performed the process of dry reforming for a long period of time without deactivation of catalyst[22,23]. Figure 2-1 shows the effect of temperature on the equilibrium conversion at various pressures.

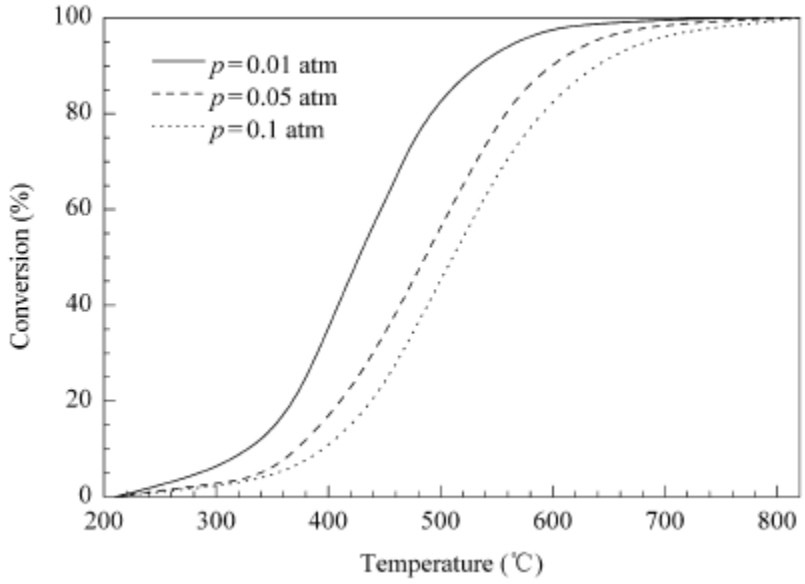

Figure 2-1: Temperature effect on equilibrium conversion for molar ratio of feed CH_4/CO_2=1/1 at different pressures [23]

2.1.2 Oxidative coupling of methane

By indirect conversion process of methane, it is converted into higher hydrocarbon which is a very high energy chemical reaction. So, oxidative coupling of methane is very promising technique which is a direct method for the production of higher hydrocarbons[23].

$$2CH_4 + 0.5O_2 \Leftrightarrow C_2H_6 + H_2O \qquad (2)$$

$$C_2H_6 + 0.5O_2 \Leftrightarrow C_2H_4 + H_2O \quad (3)$$

According to undesired behavior of this process which is due to a side reaction, yield of C_{2+} for this process is limited to almost 25% for single pass which is not good form commercial point of view. Therefore, an alternative oxidant like CO_2 is necessary for conversion of methane to higher hydrocarbons[23,24]. Chemical reaction for this process is as follow

$$2CH_4 + CO_2 \Leftrightarrow C_2H_6 + CO + H_2O \quad (4)$$

$$2CH_4 + 2CO_2 \Leftrightarrow C_2H_4 + 2CO + 2H_2O \quad (5)$$

According to thermodynamic analysis for equilibrium conversion, yield of C_{2+} hydrocarbon is 30% at 800 ^{o}C[23,25]. On the other hand, recent practical results have been shown that yield of this reaction is below 10%. Therefore, a new technique is used for the production of higher hydrocarbons which is the combination of normal OCM and CO_2 OCM. In this technique, barium titanate is used as a catalyst and yield of C_{2+} hydrocarbon is almost 30%. Figure 2-2 shows the results of barium titanate catalyst[23].

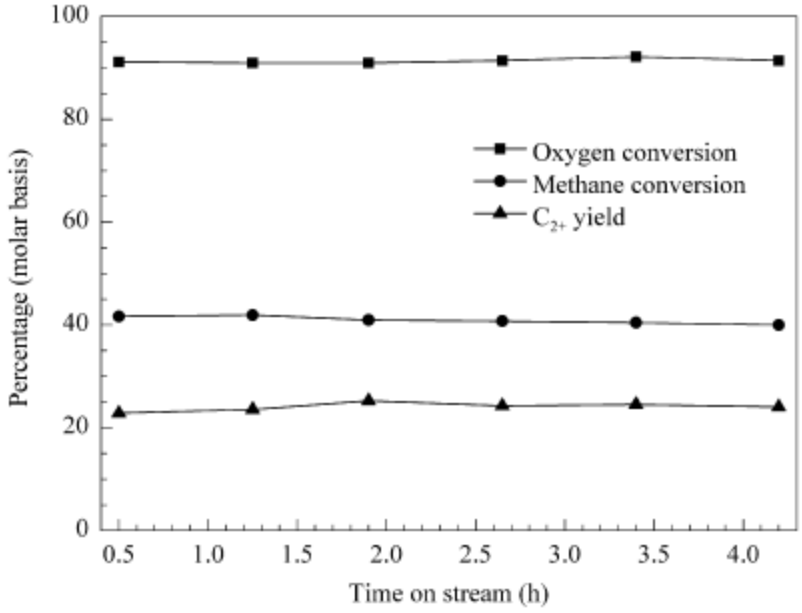

Figure 2-2: Results of barium titanate catalyst at GHSV= 3300 h^{-1}, T=1050 K and feed ratio $CH_4:CO_2:O_2:N_2$=2:2:1:1 [23]

2.1.3 Oxidative dehydrogenation

By dehydrogenation of hydrocarbons, paraffins can be converted into olefins in the presence of a catalyst. It is an equilibrium limited and endothermic reaction. During this reaction, hydrogen is produced which is converted into water due to oxidation of hydrogen. Because of this reason, yield of product is very high. Therefore, Styrene can be produced by dehydrogenation of ethyl-benzene.

$$C_6H_5C_2H_5 \Leftrightarrow C_6H_5C_2H_3 + H_2 \quad (6)$$

Due to high energy cost of steam or oxygen, an alternate approach is used in which CO_2 is utilized as oxidant. The reaction of this process is shown below

$$C_6H_5C_2H_5 + CO_2 \Leftrightarrow C_6H_5C_2H_3 + CO + H_2O \quad (7)$$

Mimura et al. compared the energy required for both process and concluded that energy required for production of styrene from ethyl benzene using commercial process and CO_2 process in the presence of Fe_2O_3-Al_2O_3 is 1.5×10^9 cal/t styrene and 6.3×10^8 cal/t styrene, respectively. Therefore, it is clear that CO_2 process is economical as compared to commercial process[23,26].

Similarly, propylene can be produced from propane by using oxidative dehydrogenation process and CO_2 process[23,25].

$$C_3H_8 + 0.5O_2 \Leftrightarrow C_3H_6 + H_2O \quad (8)$$

$$C_3H_8 + CO_2 \Leftrightarrow C_3H_6 + CO + H_2O \quad (9)$$

Figure 2-3 and 2-4 shows the process flow diagram for both processes.

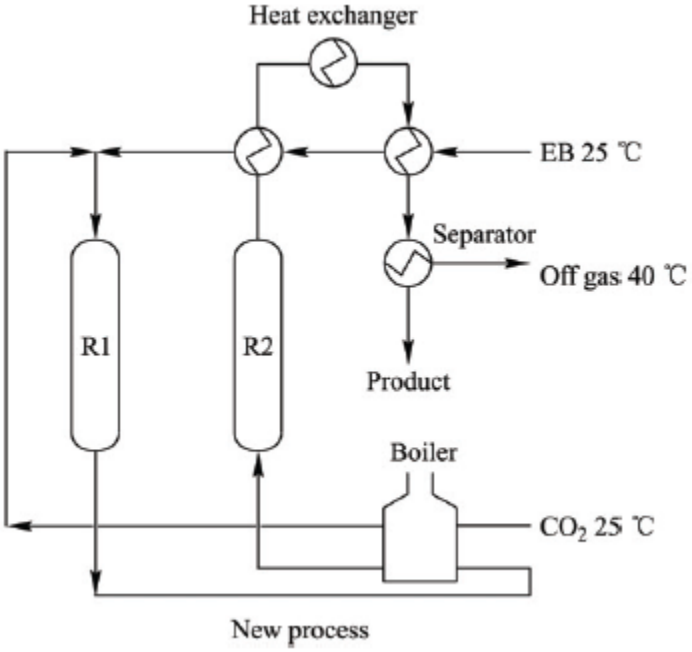

Figure 2-3: Process flow diagram for production of styrene from CO_2 process[23]

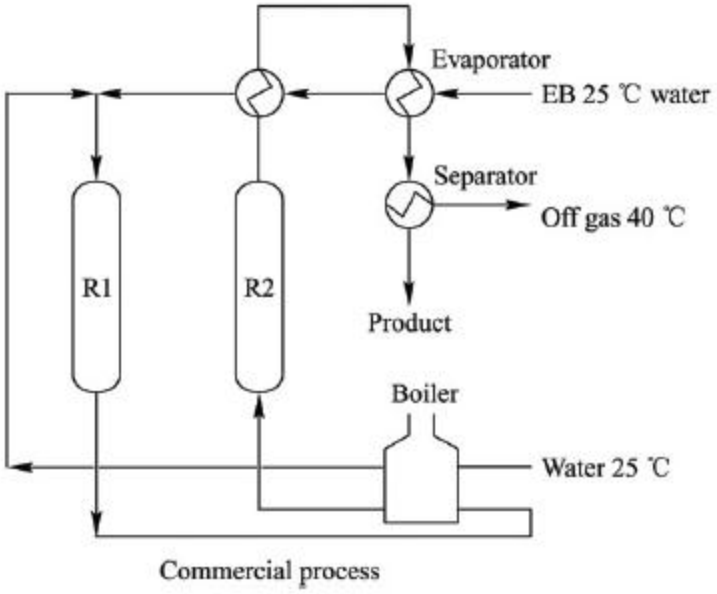

Figure 2-4: Process flow diagram for production of styrene from commercial process[23]

2.1.4 Synthesis of urea and urethane derivatives

In industry, urea is produced by using ammonia in a reaction scheme. Actually, carbon dioxide has the tendency that it is promptly reacted with nucleophiles. By using the method of dehydrogenation, alternate urea can be produced. For instance, hydrophilic ionic liquids is used as a reaction media and water is removed for the production of N,N'-dialkylurea (Eq.(10))[9,27]. On the contrary, CO_2 is used for production of carbamic acids. In this process, CO_2 is reacted with primary or secondary amine and carbamic acids are produced (Eq.(11))[9]. Further, Carbamic acid is reacted with organic halides for synthesis of urethanes (Eq.(12)). Urethanes can also be formed by the reaction of carbamic acid with alcohols instead of organic halides (Eq.(13)). According to environment point of view, this process is more suitable because water is produced as a by-product[28,29]. But according to thermodynamic limitations, the yield of this process is very low as well as catalyst is deactivated due to water. For production of urethanes,

there are a number of heterogeneous as well as homogeneous catalysts which are used for this process[9,30].

$$2R^1R^2NH + CO_2 \longrightarrow R^1R^2N - CO - NR^1R^2 + H_2O \quad (10)$$

$$R^1R^2NH + CO_2 \leftrightarrows R^1R^2NCO_2H \overset{base}{\Longleftrightarrow} [R^1R^2NCO_2]^- + [(base)H]^+ \quad (11)$$

$$RNH_2 + CO_2 + R^1X + base \longrightarrow RNHCO_2R' + HX(base) \quad (12)$$

$$RNH_2 + CO_2 + R^1OH \longrightarrow RNHCO_2R' + H_2O(base) \quad (13)$$

2.1.5 Synthesis of carboxylic acid

Carboxylic acid can also be produced by utilization of CO_2.For production of carboxylic acid, reaction of CO_2 with organic substrates is carried out in the presence of transition metals. There are very few cases in which carboxylic acid is produced from direct C-H carboxylation by using CO_2. On the other hand, it is produced from a stepwise approach in which the combination of activation of C-H and fixation of CO_2 is used and carboxylic acid is synthesized[4].

$$R - H + CO_2 \longrightarrow R - COOH \quad (14)$$

From a long time, production of carboxylic acid from direct catalytic C-H carboxylation has got a great importance. In these days, C-H bonds are activated by using different transition metal catalysts like Pd, Ir, Rh, Pt and Au for production of carboxylic acid. V or Pd based catalysts are used for the synthesis of acetic acid. During this reaction, CH_4 is reacted with CO_2 in the vicinity of V or Pd based catalysts whereas $K_2S_2O_8$ is used as a oxidizing agent in this reaction. The yield of this process is 7% [4].

$$CH_4 + CO_2 + SO_3 \longrightarrow CH_3CO_2SO_3H \quad (15)$$

$$CH_3CO_2SO_3H \longrightarrow CH_3CO_2H + SO_3 \quad (16)$$

Similarly, acrylic acid can also be produced by reacting ethylene with CO_2 in the presence of an efficient catalyst (Eq.(17)) [9,31].

$$H_2C = CH_2 + CO_2 \longrightarrow H_2C = CHCO_2H \quad (17)$$

2.1.6 Hydrogenation of CO_2

During hydrogenation of CO_2, it is reacted with hydrogen in the presence of a metal-catalyst and converted the CO_2 into methanol, dimethyl ether, methane and other hydrocarbons. The type of product is highly dependent on the operating conditions and type of catalyst[9,23]. Actually, hydrogen has very high energy because of which it can easily react with CO_2 and converted it into valuable products. Due to future energy carrier, methanol and dimethyl ether have been got a great attention[9]. Overall, products from hydrogenation of CO_2 can be divided into two major classes which are fuel and chemicals[3,9]. Wang et al. has been explained that catalytic hydrogenation is the best process for conversion of CO_2[6,9].

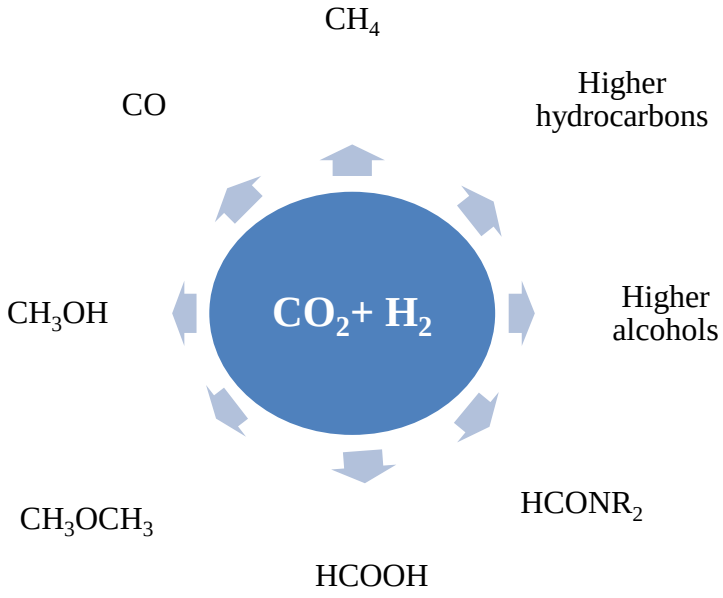

Figure 2-5: Products from hydrogenation of CO_2

Due to high energy consumption, fuel demand is increasing day by day. On contrary, the reservoirs of fossil fuel are declining because of which fuel price is fluctuating in present days. So, it is necessary to develop a process or resource from which alternate fuel can be produced. By hydrogenation of CO_2, it is possible to produce methanol, DME and other hydrocarbons which can be used in internal combustion engine. These fuels are also suitable for transportation and storage[3,6]. So, due to energy requirement reason, hydrogenation of CO_2 is promising process among all of these processes because it is showing the highest conversion, selectivity and yield towards hydrocarbons.

2.2 Catalytic processes for conversion of CO_2

There are three main catalytic processes for conversion of CO_2.

- Photocatalytic conversion of CO_2
- Electrochemical conversion of CO_2
- Chemical catalytic conversion of CO_2

2.2.1 Photocatalytic conversion of CO_2

In Photocatalytic reactions, reaction is carried out in the vicinity of a catalyst. Actually, Semiconductors have a vacant energy region or band gap in which upper region is filled valence band and lower region is unoccupied conduction band. Band gap energy can be defined as the difference of energy of conduction band to energy of valence band. Mathematically, it can be represented as

$$E_g = E_c - E_v \quad (18)$$

Where,

E_g= Energy of band gap

E_c= Energy of conduction band

E_v= Energy of valence band

Production of electron-hole pair occurs when an energetic photon is stroked into the semiconductor (photocatalyst). So, electron-hole pair is produced by this mechanism. Meanwhile, the energy of photon must be greater or equal to the energy of band gap of photocatalyst. Process for production of electron-hole pair is showed in (Eq.(19)). On contrary, when electron-hole pair is combined with each other, it produces heat which is showed in (eq.(20))[32].

$$Photocatalyst \overset{hv}{\rightarrow} e^- + h^+ \quad (19)$$

$$e^- + h^+ \longrightarrow heat \quad (20)$$

e^-= electron in conduction band

h^+= valence band hole

h = Planck's constant

During photocatalytic reaction, catalyst either donates an electron or absorbs an electron from the reacting media. But due to recombination of photoinduced charge, the life of bare particle of catalyst is very small. So, prevention of recombination of electron-hole pair is very critical and has a great importance. Chemical reaction must be occurred at the surface of catalyst before recombination of photoinduced charge. Phenomena of electron excitation can be demonstrated from figure 2-6. In this phenomenon, light is absorbed on the surface of catalyst and electron is excited from valence band to conduction band. Produced electron and hole could displace in so many different direction. The efficiency of electron-transfer will be enhanced if adsorption of species is held on the surface of photocatalyst. Figure 6 shows the phenomena of this process[32].

Photocatalyst and source of light are the two most important factors for a high performance of photocatalytic reaction. There are some more factors which can be influenced on the performance of photocatalytic reaction[32].

- pH has great importance in photocatalytic reactions because charge on the surface of photocatalyst is influenced by pH
- The kinetics of the reaction is influenced by the substrate concentration
- Excess of light increases the intensity of photon due to which recombination of electron-hole pair is increased

- Temperature plays a vital role because it can increase collisions which are held between the substrate and photocatalyst

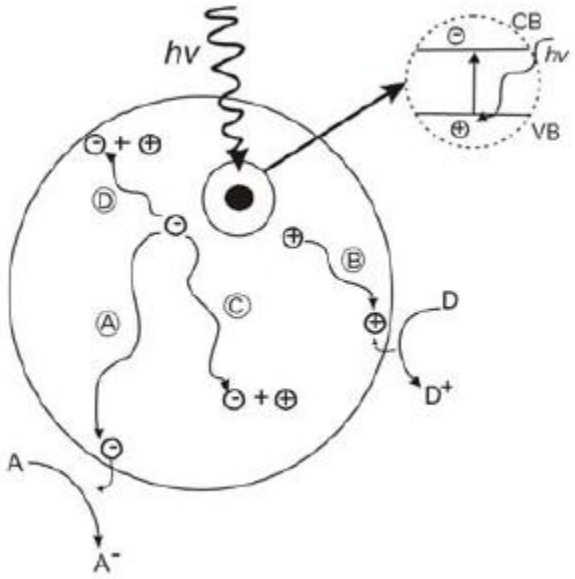

Figure 2-6: Phenomena of electron excitation and deexcitation on the surface of photocatalyst[32]

2.2.2 Electrochemical conversion of CO_2

Recently, electrochemical process is widely used for conversion of CO_2 to chemicals and fuels such as formic acid, methanol as well as other hydrocarbons. In electrochemical process, electricity is used as an energy source[33]. So, electrocatalysts or cathode materials are required for this process. Reaction is performed in the presence of these electrocatalysts or cathode materials at low potential and with high current density. Electrochemical conversion of CO_2 has the capability to handle the challenges but there are still some improvements which are needed to become this process suitable. There are two main factors for conversion of CO_2

- High energy efficiency which is the measure of energy stored in desired product as compared to energy supplied

- High current density which is necessary for designing the size of reactor

High energy efficiency is very important to avoid the excess of energy usage. Similarly, high density is also very important to avoid the large size of reactor. Therefore, by optimizing the catalyst, design of the reactor, reaction for oxidation and operating conditions, high energy efficiency and high current density can be attained. The typical operating conditions for electrochemical conversion of CO_2 are comprised of temperature, pH and electrolyte composition[9].

So, hydrocarbons or syn-gas can be produced from electrochemical reduction of CO_2. Electrochemical reactor is also called cell. Electrochemical reactor is comprised of two sections, cathode and anode. In anode, water is used and it is separated into hydrogen ions and oxygen gas as mentioned in (Eq.(21)).

$$H_2O \longrightarrow 12O_2 + 2H^+ + 2e^- \quad (21)$$

The solution which has the ions, is transferred by using a membrane and it is reached at cathode. On the other hand, CO_2 is filled into the cathode. So, it is reacted with ions and converted into water and a variety of products of carbon. Hydrogen can also be generated during this process. Figure 2-7 Shows a typical electrochemical reactor which is used for production of formate or formic acid from CO_2[9].

Reactions at cathode are given below,

$$CO_2 + H^+ + 2e^- \longrightarrow HCO_2 \quad (22)$$

$$2H^+ + 2e^- \longrightarrow H_{2(g)} \quad (23)$$

$$CO_2 + H^+ + 2e^- \longrightarrow CO_{(g)} + H_2O \quad (24)$$

Similarly, reaction at anode is given below

$$4OH^- \longrightarrow 2H_2O + O_{2(g)} + 4e^- \quad (25)$$

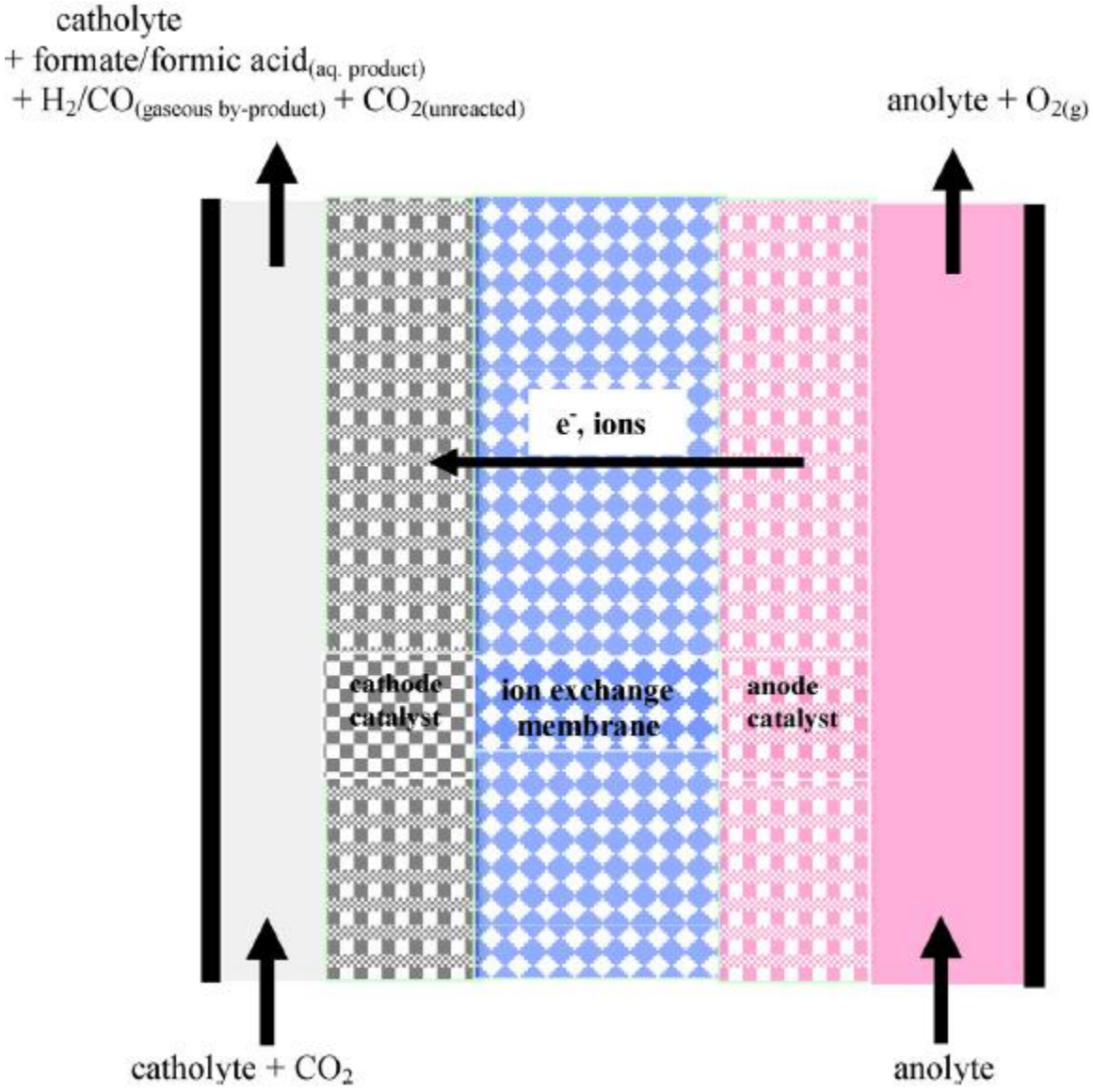

Figure 2-7: Electrochemical reactor for production of formate or formic acid from CO_2[9]

2.2.3 Chemical catalytic conversion of CO_2

In chemical catalysis, reacting substances form the bond with the catalyst and then product is produced due to reaction of these substances. Finally, after the reaction, product is detached from the catalyst. The chemical catalytic reactions can be expressed as cyclic process and for simplicity chemical catalysis is also called the catalytic reaction[34]. In heterogeneous catalytic reaction, reaction is occurred at or near the solid-fluid interface[35]. Figure 2-8 shows the mechanism of catalytic reactions.

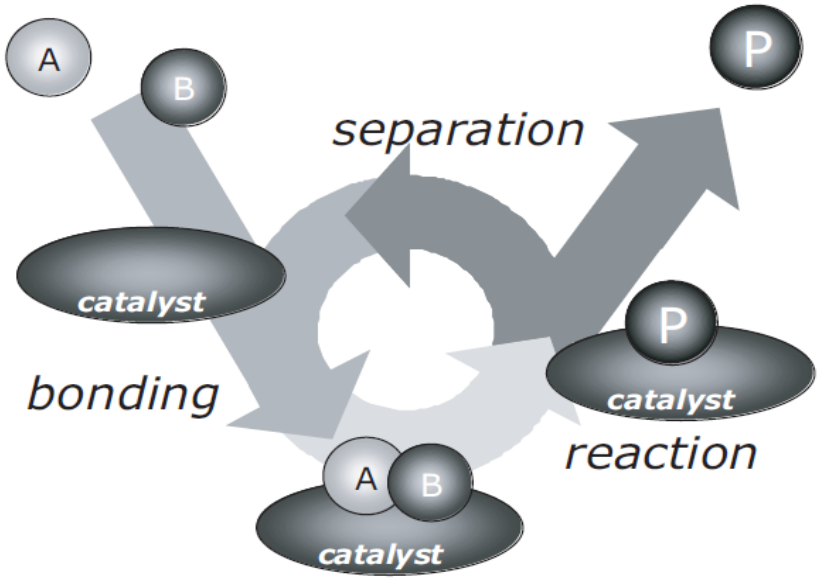

Figure 2-8: Mechanism of catalytic reaction[34]

In heterogeneous catalytic hydrogenation of CO_2, it is reacted with hydrogen in the presence of a metal-catalyst and converted the CO_2 into methanol, dimethyl ether, methane and other hydrocarbons. The type of product is highly dependent on the operating conditions and type of catalyst[9,23]. The advantage of heterogeneous catalysis is durability, handling, sequestration and reuse of catalyst as well as the design of reactor

is also played an important role. Due to advantages of heterogeneous catalysis, it has been gained much more attraction for hydrogenation of CO_2[23]. Availability of renewable hydrogen is the major disadvantage of this process. On the other hand, hydrogenation is an exothermic reaction even though at low temperature it produces a lot of heat during the reaction. For cost effectiveness, this waste heat must be controlled by thermal integration of this process[9].

2.3 Heterogeneous catalytic hydrogenation of CO_2

By using heterogeneous catalytic hydrogenation of CO_2, there are many products which can be synthesized from this process. Some of the products are discussed below.

- Production of carbon monoxide
- Production of methanol
- Production of dimethyl ether
- Production of methane
- Production of higher hydrocarbons

So, Table 2-1 is showing the different products by using different catalyst. It is also showing the conversion of CO_2 by hydrogenation of carbon dioxide.

Table 2-1: Catalysts used for conversion of CO_2

No.	Catalyst	Temperature	Pressure	Products	Conversion	Year	References
1	$Cu/ZnO/ZrO_2$+HZSM-5	340 ℃	28 atm	DME, MeOH, CO, C1-C5, C6+, Aromatics	24.50%	1995	[20]
2	$Cu/ZnO/ZrO_2$+SAPO-44	340 ℃	28 atm	DME, MeOH, CO, C1-C5, C6+, Aromatics	25.80%	1995	[20]
3	$Cu/ZnO/ZrO_2$+SAPO-5	340 ℃	28 atm	DME, MeOH, CO, C1-C5, C6+, Aromatics	25%	1995	[20]
4	$Cu/ZnO/Al_2O_3$+SAPO-5	340 ℃	28 atm	DME, MeOH, CO, C1-C5, C6+, Aromatics	24.30%	1995	[20]
5	Fe/Al_2O_3	300 ℃	2.03 Mpa	CO, C1-C5	60	1995	[36]
6	$FeMn/Al_2O_3$	300 ℃	2.03 MPa	CO, C1-C5	57.9	1995	[36]
7	$FeCo/Al_2O_3$	300 ℃	2.03 Mpa	CO, C1-C5	62.6	1995	[36]
8	$FeNi/Al_2O_3$	300 ℃	2.03 MPa	CO, C1-C5	52.7	1995	[36]
9	Fe/ Al_2O_3+MnFer	300 ℃	2.03 Mpa	CO, C1-C5	58.4	1995	[36]
10	Fe/ Al_2O_3+CoFer	300 ℃	2.03 MPa	CO, C1-C5	61.8	1995	[36]
11	Fe/ Al_2O_3+NiFer	300 ℃	2.03 Mpa	CO, C1-C5	58.2	1995	[36]
12	Fe	573K	10 atm	CO,C1, C2=,C2,C3=,C3,C4=,C4,C5+	16.21	1997	[37]
13	Fe-V	573K	10 atm	CO,C1, C2=,C2,C3=,C3,C4=,C4,C5+	11.17	1997	[37]
14	Fe-Cr	573K	10 atm	CO,C1, C2=,C2,C3=,C3,C4=,C4,C5+	25.7	1997	[37]
15	Fe-Mn	573K	10 atm	CO,C1, C2=,C2,C3=,C3,C4=,C4,C5+	23.15	1997	[37]
16	Fe-Zn	573K	10 atm	CO,C1, C2=,C2,C3=,C3,C4=,C4,C5+	26.54	1997	[37]

17	Fe-K/ (Al_2O_3:MgO(100:0)	573 K	10 atm	CO, C1, C2=,C2,C3=,C3,C4=,C4,C5+	21.34%	1998	[21]
18	Fe-K/ (Al_2O_3:MgO(90:10)	573 K	10 atm	CO, C1, C2=,C2,C3=,C3,C4=,C4,C5+	24.05%	1998	[21]
19	Fe-K/ (Al_2O_3:MgO(80:20)	573 K	10 atm	CO, C1, C2=,C2,C3=,C3,C4=,C4,C5+	27.50%	1998	[21]
20	Fe-K/ (Al_2O_3:MgO(70:30)	573 K	10 atm	CO, C1, C2=,C2,C3=,C3,C4=,C4,C5+	23.08%	1998	[21]
21	Fe-K/ (Al_2O_3:MgO(50:50)	573 K	10 atm	CO, C1, C2=,C2,C3=,C3,C4=,C4,C5+	18.79%	1998	[21]
22	Fe-K/ (Al_2O_3:MgO(25:75)	573 K	10 atm	CO, C1, C2=,C2,C3=,C3,C4=,C4,C5+	16.83%	1998	[21]
23	Fe-K/ (Al_2O_3:MgO(0:100)	573 K	10 atm	CO, C1, C2=,C2,C3=,C3,C4=,C4,C5+	13.75%	1998	[21]
24	Fe/HY	573 K	10 atm	C1, C2=,C2,C3=,C3,C4=,C4,C5+	10.14%	1999	[18]
25	Fe/LiY	573 K	10 atm	C1, C2=,C2,C3=,C3,C4=,C4,C5+	17.15%	1999	[18]
26	Fe/NaY	573 K	10 atm	C1, C2=,C2,C3=,C3,C4=,C4,C5+	20.76%	1999	[18]
27	Fe/KY	573 K	10 atm	C1, C2=,C2,C3=,C3,C4=,C4,C5+	17.95%	1999	[18]
28	Fe/RbY	573 K	10 atm	C1, C2=,C2,C3=,C3,C4=,C4,C5+	17.24%	1999	[18]
29	Fe-K/ɣ- Al_2O_3	573 k	10 atm	CH_4, C2-C4, C5-C11,C12+		2009	[19]
30	Pd/SiO_2	450 ℃	1 atm	CH_4,CO	40.8	2009	[38]
31	Pd(Imp)/SiO_2	450 ℃	1 atm	CH_4,CO	40.6	2009	[38]
32	Mg/SiO_2	450 ℃	1 atm	CH_4,CO	0.8	2009	[38]
33	Pd–Mg/SiO_2	450 ℃	1 atm	CH_4,CO	59.2	2009	[38]
34	Mg(Imp)/Pd/SiO_2	450 ℃	1 atm	CH_4,CO	40	2009	[38]

35	$Pd–Fe/SiO_2$	450 ℃	1 atm	CH_4,CO	44.7	2009	[38]
36	$Pd–Ni/SiO_2$	450 ℃	1 atm	CH_4,CO	50.5	2009	[38]
37	Ni/SiO_2	450 ℃	1 atm	CH_4,CO	36.8	2009	[38]
38	$Pd–Li/SiO_2$	450 ℃	1 atm	CH_4,CO	42.6	2009	[38]
39	$Pt-Co/ɣ-Al_2O_3$	483 K	19.9 bar	C1-C4, C5+	30%	2011	[17]
40	$CuO-Fe_2O_3-ZrO_2$/HZSM-5	260 ℃	3 MPa	DME	28.40%	2013	[1]
41	$Pt-Co/ɣ-Al_2O_3$	573 K	30 Torr	CH_4	10%	2013	[5]
42	$Pt-Co/CeO_2$	573 K	30 Torr	CH_4	10%	2013	[5]
43	Fe/Al_2O_3	573 K	1.1 MPa	CO, CH_4,C2+	12.10%	2013	[39]
44	$Fe-Co(0.10)/Al_2O_3$	573 K	1.1 MPa	CO, CH_4,C2+	20.30%	2013	[39]
45	$Fe-Co(0.17)/Al_2O_3$	573 K	1.1 MPa	CO, CH_4,C2+	25.20%	2013	[39]
46	$Fe-Co(0.25)/Al_2O_3$	573 K	1.1 MPa	CO, CH_4,C2+	26.80%	2013	[39]
47	$Fe-Co(0.50)/Al_2O_3$	573 K	1.1 MPa	CO, CH_4,C2+	33.10%	2013	[39]
48	Co/Al_2O_3	573 K	1.1 MPa	CO, CH_4,C2+	48.80%	2013	[39]
49	$Fe/K(0.3)/Al_2O_3$	573 K	1.1 MPa	CO, CH_4,C2+	27.00%	2013	[39]
51	$Fe-Co(0.10)/K(0.3)/Al_2O_3$3	573 K	1.1 MPa	CO, CH_4,C2+	35.80%	2013	[39]
52	$Fe-Co(0.17)/K(0.3)/Al_2O_3$	573 K	1.1 MPa	CO, CH_4,C2+	33.70%	2013	[39]
53	$Fe-Co(0.17)/K(0.5)/Al_2O_3$	573 K	1.1 MPa	CO, CH_4,C2+	33.60%	2013	[39]

54	Fe-Co(0.17)/K(1.0)/Al_2O_3	573 K	1.1 MPa	CO, CH_4,C2+	31.00%	2013	[39]
55	Fe-Co(0.25)/K(0.3)/Al_2O_3	573 K	1.1 MPa	CO, CH_4,C2+	32.00%	2013	[39]
56	Fe-Co(0.50)/K(0.3)/Al_2O_3	573 K	1.1 MPa	CO, CH_4,C2+	50.30%	2013	[39]
57	Co/K(0.3)/Al_2O_3	573 K	1.1 MPa	CO, CH_4,C2+	60.60%	2013	[39]
58	Fe-Mn-K/Al_2O_3	573 K	1.1 MPa	CO, CH_4,C2+	19.40%	2013	[39]
59	K/Fe-Cu-Al	320 ℃	10 bar	CH_4,C2=,C3=,C4=,C5=		2013	[15]
60	K/Mn/Fe/Al_2O_3			C1-C6	38.10%	2013	[2]
61	K/Mn/Fe/Al_2O_3-TEOS			C1-C6	31.20%	2013	[2]
62	Fe-Cu-K-Al	250-350 ℃	1-4 Mpa	C1, C2=,C2,C3=,C3,C4=,C4	32.20%	2014	[3]

2.3.1 Production of carbon monoxide

Carbon dioxide can be converted into carbon monoxide by reverse water gas shift reaction. It is an endothermic reaction because of which carbon monoxide reaction is occurred at high temperature[6,9]. On the other hand, copper based catalysts are thermally unstable at high temperature because these catalysts are deactivated at high temperature due to sintering of the catalyst. So, thermal stabilizers are used with copper to maintain the stability of these catalysts at high temperature. For this purpose, Iron is mostly used for the activity and stability of Cu/SiO_2 catalyst at high temperature and it is noted that Cu/SiO_2 efficiency is increased in the presence of iron[40].

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (26)$$

For copper catalysts, reaction mechanism for reverse water gas shift reaction is composed of two main reaction mechanisms which are redox decomposition and formate decomposition. This mechanism can be illustrated from Eq.(27) & Eq.(28)[6,9]. So, for dissociation of CO_2, Cu^o shows good activity for this. On contrary, the reduction of this oxidized catalyst is too much fast as compared to the oxidization of this process. Hydrogen is acting as a reducing reagent during this process and it does not play any role during intermediates formation for the process of reverse water gas shift reaction[6,9].

$$CO_2 + 2Cu^o \longrightarrow Cu_2O + CO \quad (27)$$

$$Cu_2O + H_2 \longrightarrow 2Cu^o + H_2O \quad (28)$$

Cu- Fe catalyst which is used for production of CO, gives a very large surface area for this reaction. For preheating at high temperature, it also shows the stability of catalyst.

The activity of Cu-Fe catalyst is noted stable and efficient till 120 h for operating conditions 600 ^{o}C and atmospheric pressure[40].

2.3.2 Production of methanol

According to industrial point of view, methanol is very important because it has large applications in chemical industry. It is used as solvent, fuel as well as raw material for other chemicals. CO_2 is good alternative for production of methanol because of which CO is replaced with CO_2. Therefore, Conversion of CO_2 to methanol is very promising technique regarding to utilization of CO_2[41].

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad (29)$$

According to Liu et al., molybdenum sulfide cluster is used for conversion of CO_2 to CO by reverse water gas synthesis mechanism and HOCO intermediates (Figure 2-9) are formed during this reaction. By hydrogenation of CO, it is converted into HCO radicals which are further converted into methanol. For overall reaction, HCO radical production reaction is the main rate determining step. CO_2, CO and CH_xO are chemisorbed on the molybdenum (Mo). Meanwhile, sulfur (S) participates in the breaking of H-H bond[42].

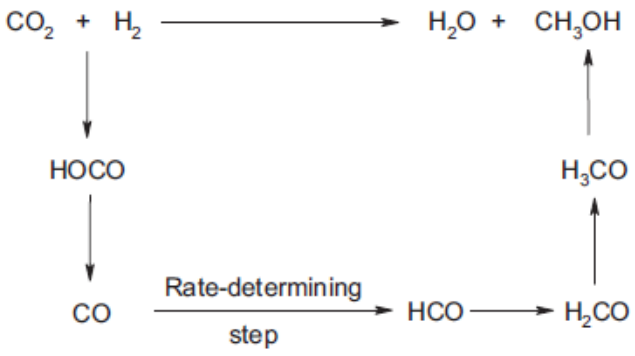

Figure 2-9: Reaction pathways for hydrogenation of CO_2 to methanol on Mo_6S_8[6,9]

It is so far believed that $Cu/Zn/Zr_2$ catalyst which is used for production of syngas. It can also be used for the production of methanol from hydrogenation of CO_2 because it shows good activity towards the production of methanol. It is also used for the production of methanol through steam reforming[9,43]. However, different oxides are used to modify the catalyst which has the characteristic of enhancing the stability and activity of the catalyst. For this purpose, irreducible oxides like Al_2O_3, TiO_2 and Ga_2O_3 are widely studied to improve the activity and stability of catalyst towards methanol production[44]. Meanwhile, different metals like boron, chromium, tungsten and manganese have also been checked. Several metal oxide additives such as VO_x, MnO_x and MgO have also been investigated. Similarly, different basic oxides like La_2O_3 which are used as support for palladium (Pd) and SiO_2 support for lithium promoted Pd have also been showed a good selectivity and activity towards methanol production[9].

2.3.3 Production of dimethyl ether

Recently, it is believed that Dimethyl ether is a good substitute for the diesel because it has low NO_x emission, high cetane number and almost smoke free combustion of DME. So, combustion performance of Dimethyl ether is better than diesel[9]. Essentially, there are two processes for the production of DME from CO_2 and H_2. (1) Two-step process. (2) One step process. In two step process, firstly methanol is produced and afterward, by dehydration of methanol, DME is synthesized. On contrary, when methanol and dehydration of methanol to produce DME is carried out in a single step then it is called single step process[1].

Therefore, researchers are focusing on the one step process because of the two main reasons. (i) The production of the methanol and DME in one step obstructs the methanol

intermediate as it cause hindrance for methanol production in the reactor (ii) On economic point of view, in one step process, only one reactor is required which reduces the cost for DME production. So, for this purpose, a bifunctional catalyst is used to synthesize DME. This bifunctional catalyst has the characteristic that it is useful for hydrogenation of CO_2 to produce methanol and dehydration of methanol to produce DME[1,15]. CuO-ZnO over HZSM-5 or HY zeolite is used as catalyst. Therefore, CuO-ZnO serves as hydrogenation component and HZSM-5 helps in dehydration of methanol to produce DME[1,9,45]. There are four main reactions during the synthesis of DME.

$$CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O \quad (30)$$

$$CO_2 + H_2 \leftrightharpoons CO + H_2O \quad (31)$$

$$CH_3OH \leftrightharpoons CH_3OCH_3 + H_2O \quad (32)$$

$$CO_2 + 4H_2 \leftrightharpoons CH_4 + 2H_2O \quad (33)$$

2.3.4 Production of methane

Sabatier reaction is a very important catalytic process because it is used for the production of methane from catalytic hydrogenation of CO_2. Consequently, syngas and compressed natural gas can be produced from catalytic hydrogenation of CO_2 by using Sabatier reaction process[6,9].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (34)$$

According to thermodynamic point of view, production of methane from hydrogenation of CO_2 is an agreeable approach but it has significant kinetic limitations. Actually, it is an eight electron process for the reduction of fully oxidized carbon to methane. So, it

demands a promising catalyst which has good selectivity, rate and conversion towards methane[6,9,38]. The mechanism for methanation of carbon dioxide by using synthesized catalyst can be understood through figure 2-10.

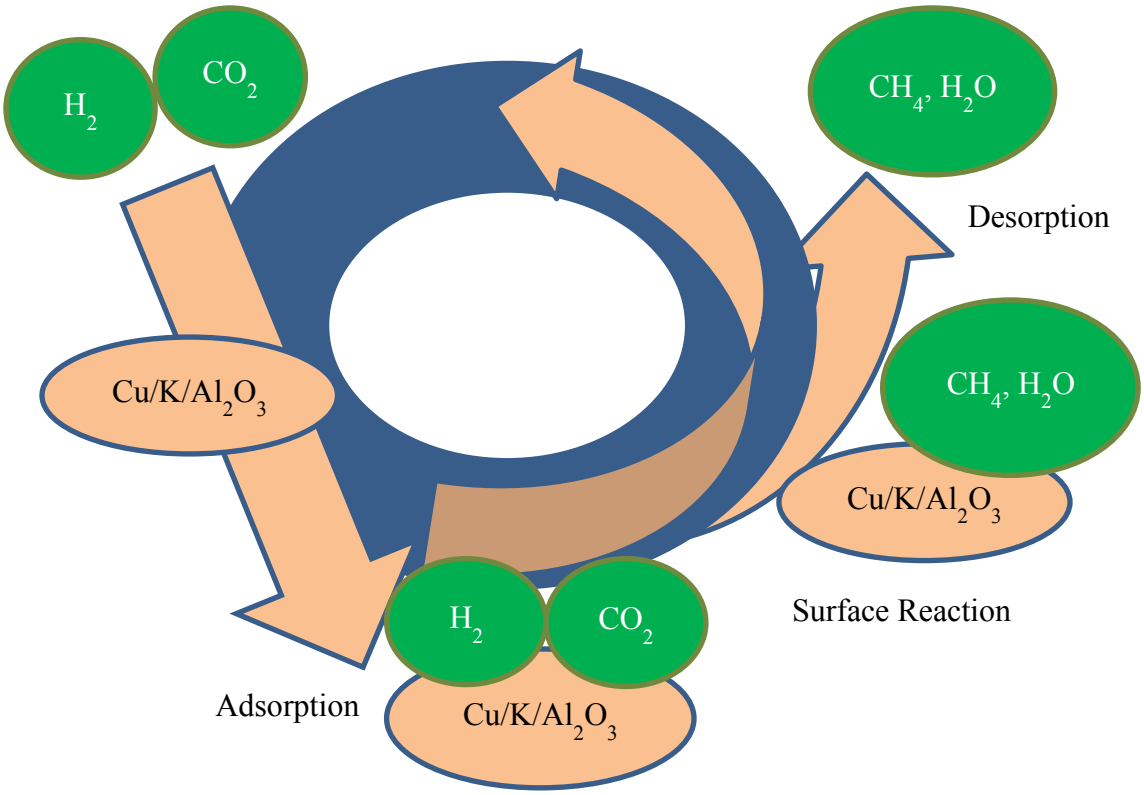

Figure 2-10: Mechanism for methanation of carbon dioxide

Different catalysts have been synthesized for hydrogenation of CO_2 to methane. These catalysts are based on VIIIB metals like Ru and Rh over different oxide supports such as TiO_2, Al_2O_3, SiO_2, CeO_2 and ZrO_2. Meanwhile, supported nickel catalysts have great importance for production of methane from CO_2 because supported nickel catalysts have high surface area and usually oxides. So, supported nickel catalyst is used extensively for synthesis of metal catalysts. On the other hand, support for nickel catalyst is very important because it decides the interaction between the support and nickel. It also estimates the catalyst performance through selectivity and activity of catalyst for

production of methane by hydrogenation of CO_2[46]. According to Chang et al., amorphous silica support for nickel catalyst shows good activity towards methane production from CO_2[47–49].

2.3.5 Production of higher hydrocarbons

Hydrocarbons can be produced by the hydrogenation of CO_2. For hydrocarbons production, hydrogenation of CO_2 is carried out by direct or indirect routes like synthesis gas or formation of methanol intermediates[3]. Meanwhile, direct and indirect routes are also called non-methanol mediated and methanol mediated reactions respectively[3,6]. Similarly, by modification of Fisher-Tropsch Synthesis (FTS) reaction, CO_2 is converted into hydrocarbons. In modified FTS reaction, CO_2 is used for production of hydrocarbons instead of CO. Catalyst for hydrogenation of CO_2 is comparable as used in FTS reaction. However, It is modified to achieve the maximum production of hydrocarbons[6,9].

For methanol mediated reaction, Cu-Zn based catalysts are mostly used and converted the CO_2 into methanol by hydrogenation which is further converted into hydrocarbons like gasoline[50]. So, by using this approach, light alkanes are produced as major product. On contrary, for non-methanol mediated approach, hydrogenation of the CO_2 is carried out in two step process[3,6]. (1) Production of CO which is due to reverse water gas shift reaction (RWGSR). (2) Hydrogenation of CO_2 which is carried out due to modified FTS reaction[2,39]. By hydrogenation, light olefins can be produced. Meanwhile, methane can also be produced directly.

$$nCO_2 + nH_2 \leftrightarrows nCO + nH_2O \quad (35)$$

$$nCO + nH_2 \leftrightarrows (CH_2)_n + nH_2O \quad (36)$$

$$nCO_2 + 3nH_2 \leftrightarrows (CH_2)_n + 2nH_2O \quad (37)$$

From a long time, Iron oxide is used as catalyst for FTS reactions which shows good stability and activity for RWGS and WGS reactions. Due to exceptional olefinic nature of the iron based catalyst, it is used for hydrogenation of CO_2 to obtain the hydrocarbon[3,6,9]. Fe has high performance towards hydrocarbons synthesis in sufficient supply of H_2.Matsumoto et al. explained that in the presence of insufficient supply of H_2, carbon deposition is increased. Meanwhile, in the presence of the sufficient supply of the H_2, the carbon deposition will be less and performance of the catalyst will be high[2].

Similarly, Co is also widely used as a catalyst for FTS reactions which is due to its low cost and high performance. So, switching from CO to CO_2, Co is acted as a methanation catalyst rather than FTS reaction catalyst[51,52]. According to Akin et al., Co/Al_2O_3 shows 70% of methane during hydrogenation of CO_2[51]. Figure 2-11 provides a better understanding for product distribution during hydrogenation of CO and CO_2[3,6].

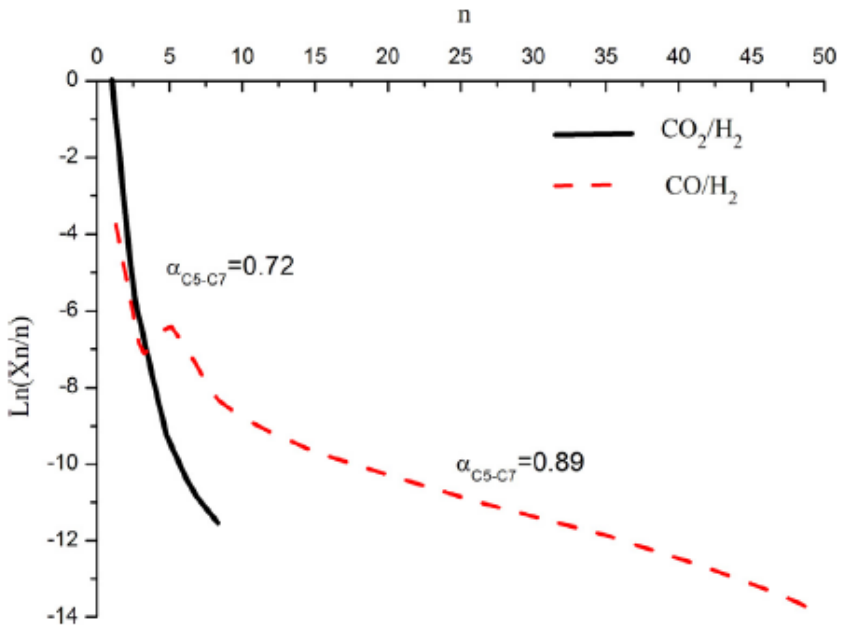

Figure 2-11: ASF plot for selectivity of hydrocarbons during the hydrogenation of CO_2 and CO [3,6]

According to Anderson-Schulz-Flory (ASF) diagram, hydrocarbons selectivity and distribution during hydrogenation of CO_2 is quite different from the hydrogenation of CO. Due to slow adsorption of CO_2 on the surface of catalyst, the product from hydrogenation of CO_2 has low C/H ratio. So, it leads towards the hydrogenation of surface adsorbed intermediates because of which chain growth of product is decreased e.g. methane formation[6].

2.3.5.1 Reaction mechanism for modified Fisher Tropsch Synthesis reaction

The mechanism for production of hydrocarbons through modified FTS reaction can be illustrated from the figure 2-12. Lee et al. proposed this reaction mechanism for production of hydrocarbons through CO_2 hydrogenation. According to reaction mechanism, Iron (II) reduces the CO_2 and then formed H radicals which are further adsorbed on the surface of catalyst. The remaining H radicals strike and produce the OH

formic acid, carbonyl C and CO respectively. Similarly, carbon-carbon chain propagation is formed due to Fe-CH_2 radicals. For higher hydrocarbons, carbon-carbon chain growth is very crucial and has great importance. For modified FTS reaction, major route during production of higher hydrocarbons is carbon-carbon chain growth. Limited H_2 supply is used to transfer the selectivity of paraffin into α-olefin. Figure 2-12 shows the mechanism of modified FTS reaction for production of hydrocarbons through CO_2 hydrogenation[3].

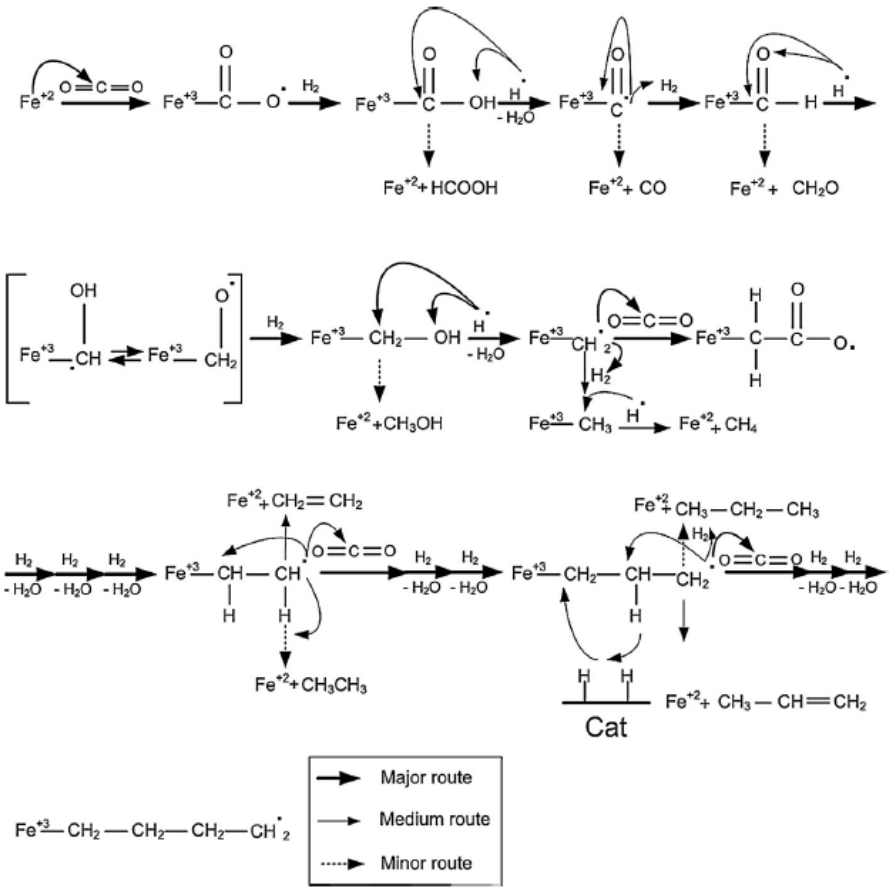

Figure 2-12: Reaction mechanism for hydrogenation of CO_2[3]

2.3.5.2 Effects of operating conditions on CO_2 hydrogenation to hydrocarbon

There are three main operating conditions which have been studied experimentally during the production of hydrocarbons from CO_2 hydrogenation. These include

- Space velocity
- Pressure
- Temperature

So, effects of these operating conditions has been investigated and presented below.

- **Effect of Space velocity**

HC yield can be increased by reducing the space velocity because residence time is increased at low space velocity due to which conversion of CO_2 and HC yield is enhanced. Meanwhile, production of water is also increased which leads towards oxidation of metallic iron. So, for best performance during hydrogenation of CO_2 can be achieved by using series of reactor in which first reactor has space velocity = 2000 and second has space velocity = 1000. Similarly, for single reactor, space velocity must be 1000 to achieve the better conversion. Therefore, space velocity is very important for high conversion of CO_2[3].

- **Effect of Pressure**

It is obvious that space velocity plays an important role for high conversion and yield but pressure is also very important because at high pressure, the carbon-carbon chain growth and HC yield is increased for CO_2 hydrogenation to hydrocarbons. On contrary, olefin/paraffin ratio is decreased at high pressure. Due to reversible nature of RWGS

reaction, high pressure has no significant effect on the conversion of CO_2 unless FTS reaction consumes the produced CO. On the other hand, FTS reaction is irreversible in nature and produces less product molecules as compared to reactants. During FTS reaction, water is produced which is unfavorable for RWGS reaction due to which conversion of CO_2 is decreased. The Mossbauer spectroscopic shows that Fe_3O_4 is acted as a dominant phase during the used catalyst for elevated reaction pressure. Although, high conversion and HC yield can be achieved at high pressure but during FTS and RWGS reaction at high pressure, water is produced which can increase the partial pressure of water on the surface of catalyst bed. So, solution of in situ removal of water is very important[3].

- **Effect of temperature**

Conversion of CO_2 was showed by researchers through the pattern of temperature effect on time. According to pattern, conversion was enhanced slowly by increasing the time for reaction. However, production of CO was increased at high temperature. It is believed that CO is produced through RWGS reaction so it is not astonishing because RWGS reaction is a reversible endothermic reaction. Therefore, it is a very serious matter to find a technique for resolving this thermal conflict among FTS and RWGS reaction. Meanwhile, catalyst deactivation is occurred at high temperature which is due to deposition of carbon on the surface of catalyst. Similarly, carbon-carbon chain is also broken at high temperature which is due to cracking effects at high temperature. So, CH_4 yield is increased among the hydrocarbons distribution. At high temperature, carburization is increased and olefin/paraffin ratio is also increased in hydrocarbons product distribution which is due to H-elimination effects during the breakage of carbon

chain on rich carbon surface and reaction is turned into Boudouard reaction as shown in Eq.(38). So to avoid this situation, concentration of H_2 must be adjusted[3].

$$CO + CO \longrightarrow C + CO_2 \quad (38)$$

CHAPTER 3

EXPERIMENTAL SECTION

In present section, series of Cu and K catalysts over alumina support were synthesized by using impregnation technique. Furthermore, prepared catalyst was characterized by XRD, TGA, SEM, EDXS, BET and FTIR to check the phase of catalyst, presence of deposited component on the catalyst, surface morphology and presence of catalyst over the support, Surface area and pore volume of prepared catalyst, and presence of functional group in prepared catalyst, respectively. However, fixed bed reactor was used to evaluate the performance of the catalyst during catalytic hydrogenation of carbon dioxide to convert it into methane.

3.1 Materials

Al_2O_3, $Cu(NO_3)_2.3H_2O$ and KNO_3 were used during the preparation of catalyst for conversion of CO_2 to methane. For the catalytic hydrogenation of carbon dioxide, Al_2O_3 was used as a catalyst support while $Cu(NO_3)_2.3H_2O$ and KNO_3 were utilized as the source of Cu and K metals, respectively. Al_2O_3 was purchased from Riedel-deHaën, Sigma-Aldrich. Meanwhile, $Cu(NO_3)_2.3H_2O$ and KNO_3 were purchased from Panreac. The purity of both $Cu(NO_3)_2.3H_2O$ and KNO_3 was 98%. Hence, these materials were used as purchased from these companies.

Table 3-1: Materials used for synthesis of catalysts

Material	Company	Purity
Al_2O_3	Riedel-deHaën, Sigma-Aldrich Chemie GmbH, Eschenstrasse 5, 82024 Taufkirchen, Germany	High purity
Cu	Panreac Química S.L.U., E-08211 Castellar del Vallès, (Barcelona) Spain	98%
K	Panreac Química S.L.U., E-08211 Castellar del Vallès, (Barcelona) Spain	98%

3.2 Synthesis of Catalyst

Impregnation technique is a very well-known method which can be used for the preparation of metallic and non-metallic catalysts. For conversion of CO_2, $Cu/K/Al_2O_3$ catalyst was synthesized by using impregnation method. Nitrate salts of Cu and K were dissolved in distilled water and Al_2O_3 was added in the solution. $Cu(NO_3)_2.3H_2O$, KNO_3 and Al_2O_3 were added according to the amount of Cu, K and Al_2O_3 in the $Cu/K/Al_2O_3$ catalyst. For homogeneity of mixture, it was mixed by shaking the solution for 10 min. This homogeneous mixture was kept at room temperature till 24 h for adsorption of catalyst at the surface of support. Subsequently, the prepared catalyst was filtered and dried at 110℃ in oven for 4 h with a heating rate of 16℃/min. Calcination of the prepared catalyst was carried out in muffle furnace at 550℃ for 6 h with the ramp of 5℃/min. $Cu/K/Al_2O_3$ calcinated catalyst was then stored in a sample bottle for further reaction of carbon dioxide hydrogenation.

3.3 Catalyst Characterization

3.3.1 BET

Micromeretics ASAP2020 was used to find out the porosmetric features of prepared catalyst. 0.4 g of sample was degassed for 2 hours at constant temperature of 400 K. N_2 adsorption at a temperature of 77 K was used to find the morphology of catalyst. Nitrogen volume adsorbed versus its relative pressure was recorded to find the BET surface area, t-plot micropore volume, and BJH pore size distribution of the catalyst particles.

3.3.2 FTIR

FTIR transmission spectrum was recorded between 400 cm^{-1} to 4000 cm^{-1} by using Thermo scientific Nicolet FTIR spectrometer. Sample pellet was prepared by mixing 1mg dried catalyst powder with 500mg KBr in an agate mortar and pressing the resulting mixture at 10 tonnes/cm^2 for 1min. Pellets were dried overnight at 105 ℃ before analysis to avoid interference of moisture in the recorded spectrum.

3.3.3 XRD

To identify the crystalline phases present in the prepared catalyst XRD (x-ray diffraction) analysis was conducted using Phillips diffraction Unit (Model PW 1140/90). Machine was operated with monochromatic Cu Kα radiation source at 50 mA and 40 kV. Scanning speed was set at 4º 2θ min^{-1} with a step size of 0.1º in the range of 10-80º 2θ.

3.3.4 SEM

Scanning Electron Microscope (JEOL JSM-5600) was used to get the Micrographs of catalyst. Particles first stuck to specimen stub by carbon glue and gold coated under vacuum for 60 sec. The analysis conditions were set at an accelerating voltage of 15 kV, a beam current of 1nA and a Si (Li) detector located at 10 nm away from the sample to be analyzed. X-ray detection limit was set at 0.1%.

3.3.5 TGA

Thermal gravimetric analysis or thermo gravimetric analysis is used to check weight loss of synthesized catalyst by changing the temperature. It can also predict the thermal

stability of catalyst. Therefore, approximately 40-45 mg of the spent catalyst sample was placed into an aluminum sample pan for TGA using an empty aluminum pan as a reference. For TGA analysis of synthesized catalyst, Shimadzu TGA-60 was used with a temperature range between 25 °C to 900°C at a ramp of 10 °C/min in an air atmosphere (100 ml/min). TGA analysis was accomplished to check the presence of carbon deposition on the surface of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst after reaction at 230 °C and 600 °C.

3.4 Catalytic hydrogenation of carbon dioxide

Sabatier reaction is a very important catalytic process because it is used for the production of methane from catalytic hydrogenation of CO_2. Consequently, syngas and compressed natural gas can be produced from catalytic hydrogenation of CO_2 by using Sabatier reaction process[6,9].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (39)$$

For catalytic hydrogenation of carbon dioxide, Cu/K/Al_2O_3 catalyst was packed in a fixed bed column whose length is 22.7 cm and internal diameter is 3 mm. Fixed bed column was installed in the reactor as shown in figure 3-1. Pressure and flow rate of both hydrogen and carbon dioxide gases were adjusted with the help of pressure regulators and flow meters of H_2 and CO_2. On the other hand, reduction of catalyst was performed in the reactor prior to reaction at 400℃ with a ramp of 4℃/min for 6 hr and the gas flow was 20 ml/min. Methanation of carbon dioxide was conducted at different temperatures and molar ratios of carbon dioxide to hydrogen. Therefore, both hydrogen and carbon dioxide gases were reacted in the vicinity of Cu/K/Al_2O_3 catalyst. The temperature and pressure

were adjusted at constant values of 230℃ and 7 bar. The molar ratio of H_2/CO_2 feed was also maintained at a value of 4/1. The flow rate of the outlet was fixed at 10 ml/min. Therefore, product from the outlet valve was analyzed with the help of online Agilent GC and measured the conversion of the CO_2 and selectivity of the methane. Conversion of carbon dioxide, selectivity of CH_4 and carbon monoxide were defined as follow[53,54],

$$X_{CO_2} = \frac{(F_{CO_2,out} - F_{CO_2,in})}{F_{CO_2,in}} \times 100 \quad (40)$$

$$S_{CH_4} = \frac{(F_{CH_4,out})}{F_{CH_4,out} + F_{CO,out}} \times 100 \quad (41)$$

$$S_{CO} = \frac{(F_{CO,out})}{F_{CH_4,out} + F_{CO,out}} \times 100 \quad (42)$$

On the other hand, experiments were repeated at different temperatures and molar ratios to check the effect of temperature and molar ratio on conversion of carbon dioxide. For the investigation of temperature effect on the conversion of carbon dioxide, temperature was varied as 230 ℃, 400 ℃, and 600 ℃ while other parameters were fixed. In the interim, effect of molar ratio was also probed by varying hydrogen to carbon dioxide as 4/1 and 2/1, respectively. Meanwhile, pressure and temperature were constant. Subsequently, conversion of carbon dioxide for all these parameters was calculated by analyzing the product through online Agilent GC and reported in the current paper.

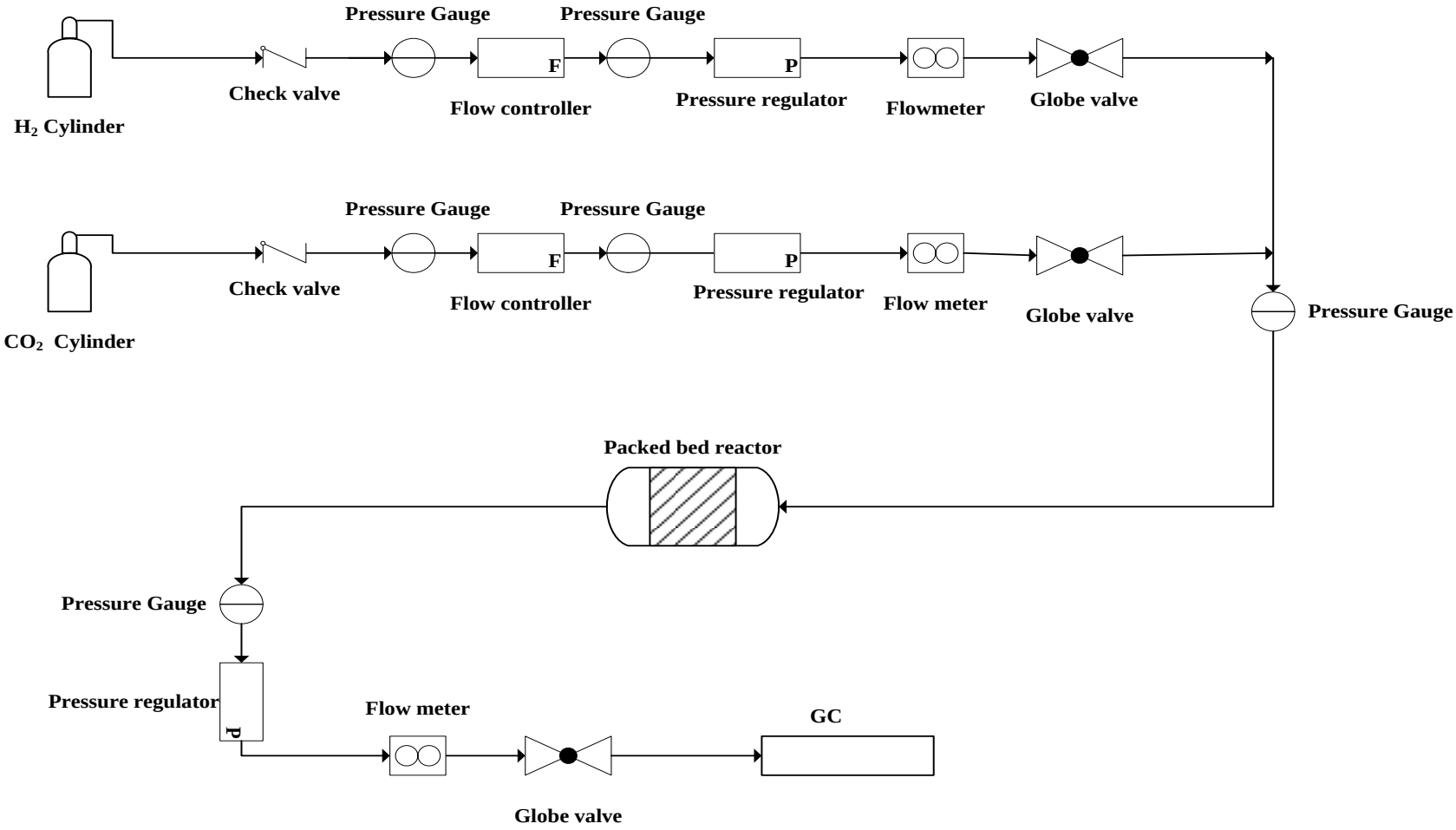

Figure 3-1: Fixed bed reactor for catalytic hydrogenation of carbon dioxide

CHAPTER 4

RESULT AND DISCUSSION

4.1 Characterization of catalyst

4.1.1 XRD technique for phase analysis

XRD technique is used to investigate the phase analysis of components in the catalyst. For this purpose, XRD analysis of reduced 1.62 wt. % Cu/(0.5)K/Al_2O_3 catalyst was performed to check the phase of components in the catalysts which is shown in figure 4-1. The presence of metallic copper is demonstrated by the peak which was appeared at about 2θ≈43° (JCPDS 01-089-2838)[55]. There is neither any characteristic peak for CuO crystalized in monoclinic structure at 2θ≈35.5° and 39°, respectively (JCPDS 05-0661) nor any poorly crystalized CuO phase was appeared at 2θ≈66° and 74.5°, respectively[55,56].

Figure 4-1 also shows broad peaks of Al_2O_3 at 2θ≈32°, 37°, 46° and 67°, respectively which were similar to the parent Al_2O_3 peaks[57,58]. One more diffraction line was observed at 2θ≈62°, indicating the presence of K_2O[57,59]. According to W. Xie et al., relationship between basicity or catalyst activity with K_2O phase was observed and it was appeared in XRD pattern. Therefore, this K_2O phase might be due to the basicity and high activity of catalyst. Basic sites of K_2O during activation process were due to the disintegration and dispersion of KNO_3 which was the main reason of strong basic sites formation. Actually, vacant sites of Al_2O_3 were captured by the K+ ions of KNO_3.

Therefore, it is concluded that increasing in number of basic sites can be persistent by increasing the amount of K_2O species at alumina support. Therefore, catalyst activity is also increased due to this fact[57].

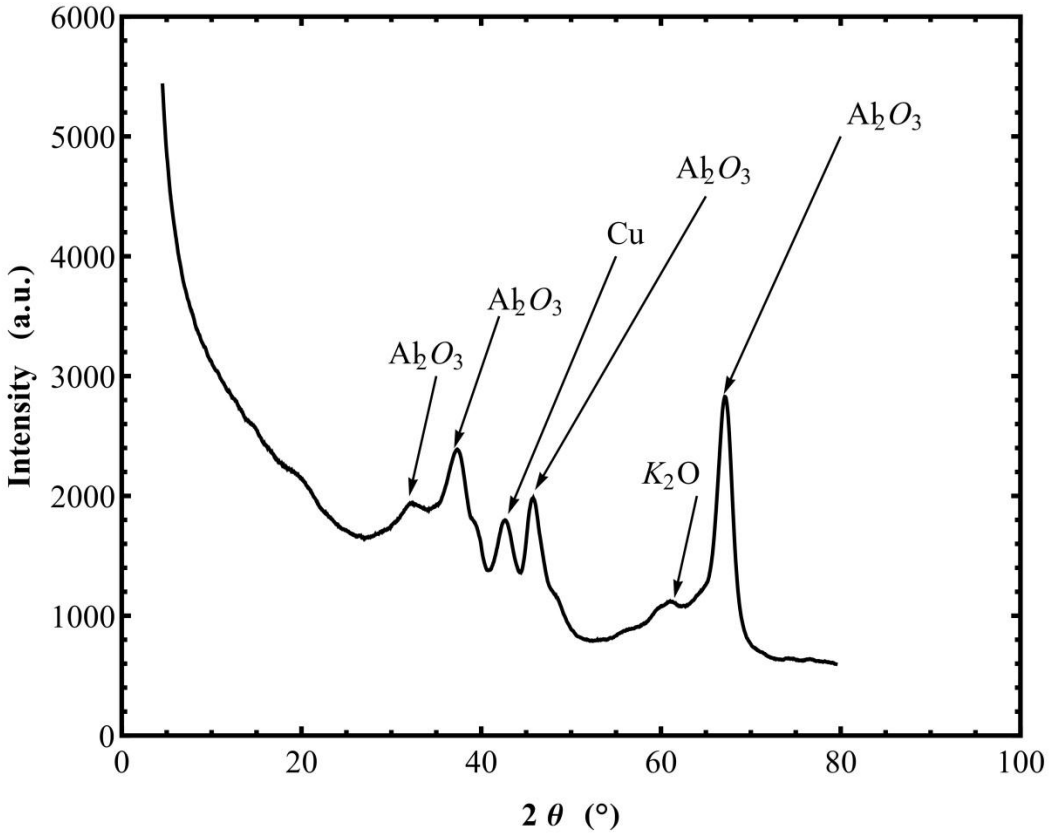

Figure 4-1: XRD analysis pattern of reduced 1.62 wt. % Cu/(0.5)K/Al_2O_3 catalyst

4.1.2 Thermo Gravimetric Analysis

Figures 4-2 and 4-3 show the weight loss and derivative weight loss TGA profiles of 1.62%Cu/K(0.5)/ Al_2O_3 catalyst after reaction at two different temperatures say 230 ℃ and 600 ℃ whereas other reaction conditions are same. It is observed that under each set of condition, there is no significant difference among the weight loss TGA profile of the used catalyst. According to figure 4-2, weight loss up to 200 ℃ was due to desorption of moisture which is absorbed by the catalyst. Similarly, it was observed that weight loss after 300 ℃ was due to the oxidation of methane which was deposited on the surface of the catalyst or carbonaceous materials which were formed during the Sabatier reaction by increasing reaction temperature. On the other hand, oxidation step of carbonaceous materials is difficult to separate from the results of TGA[15,60].

According to Botes and J.W. Bae et al., It is concluded that carbonaceous species have good reactivity for the surface bifunctional catalyst due to which derivative of weight loss peaks were appeared. From figure 4-3, it was observed that first peak for synthesized catalyst after reaction at 230 ℃ shows the low amount of methane formation which is due to the decrease of Sabatier reaction activity. This peak was appeared at 385 ℃ . The second peak was exposed at 419 ℃ which was probably due to the less active carbonaceous species on the surface of catalyst[60,61]. Similarly, weight loss is increased at higher temperature which is due to the formation of carbonaceous material at high temperature[15]. From figure 4-3, it is noted that weight of 1.62%Cu/K(0.5)/ Al_2O_3 catalyst for reaction temperature 600 ℃ is 96.63% whereas at reaction temperature 230 ℃, it is 95.81% which is due to the low selectivity of methane at 600 ℃. Subsequently, deposition of methane was decreased at the surface of catalyst for reaction temperature

600 ℃ . Hence, weight loss is less as compared to weight loss of the catalyst at reaction temperature 230 ℃. Therefore, It is concluded that observed weight loss is mainly due to deposition of methane and carbonaceous species on the surface of 1.62%Cu/K(0.5)/ Al_2O_3 catalyst.

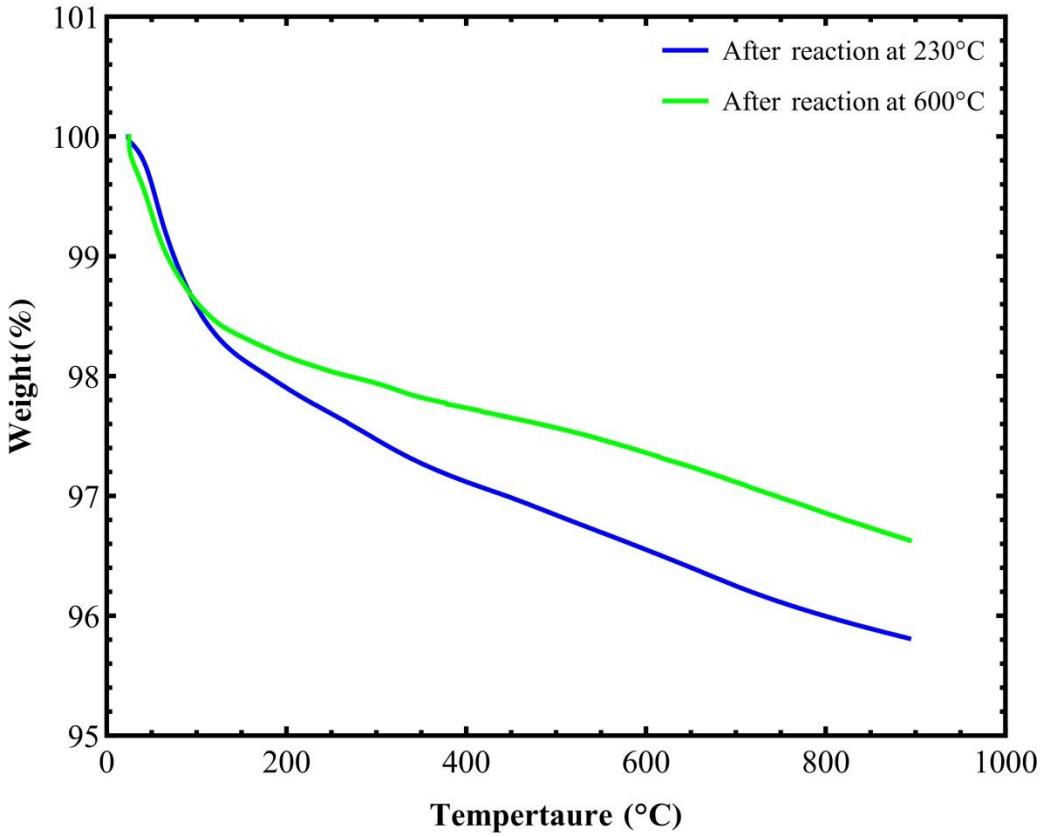

Figure 4-2: Weight loss TGA profile of 1.62%Cu/K(0.5)/ Al_2O_3 catalyst after reaction at 230 ℃ and 600 ℃ with 7 bar pressure

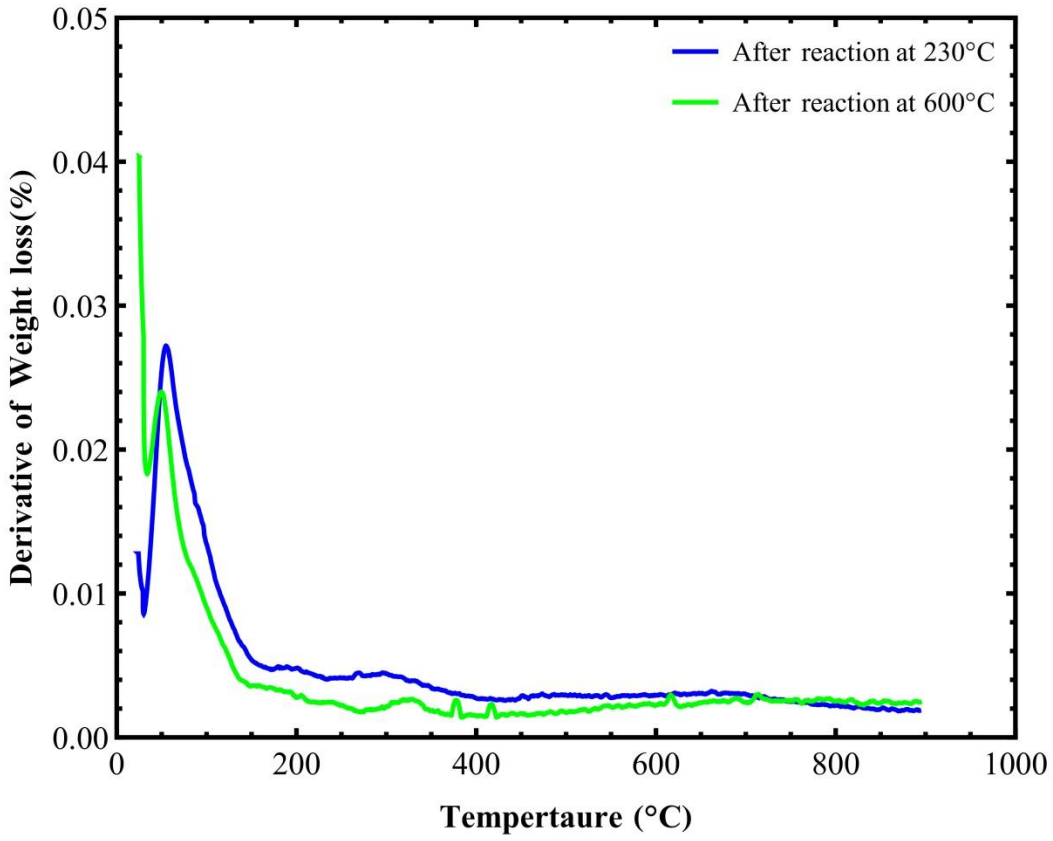

Figure 4-3: Derivative weight loss TGA profile for 1.62%Cu/K(0.5)/ Al_2O_3 catalyst after reaction at 230 ℃ and 600 ℃ with 7 bar pressure

4.1.3 Scanning electron microscopy (SEM)

Morphology feature of solid reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst can be investigated by using SEM technique. Therefore, SEM images of reduced catalyst were shown in the figures 4-5 to 4-7 at different resolutions. Back-scattered electrons are used to record the SEM images and it has advantage for compositional contrast. InLense detector was utilized for the morphology of the reduced catalyst[62]. According to figure 4-4,it can be seen that the morphology of the alumina support is irregular shaped agglomerations of particles which have clear edges. After the impregnation of Cu and K over alumina support, the morphology of Al_2O_3 and reduced solid catalyst has no significant change. Therefore, it is concluded that after the loading of copper and potassium over alumina support; the clear distinction of the alumina agglomeration could also be monitored. Due to this observation, it was suggested that preparation process of catalyst has no convincing effect on the structure of alumina support. Meanwhile, the distribution of copper and potassium compounds over alumina were homogeneous and it was critical for a good catalyst[63]. The size of catalyst was ranged between 0.09 to 0.24 nm. According to XRD and EDXS, it was concluded that cu was existed as metallic copper and K was presented as K_2O in the catalyst[62].

By using the Scherrer equation, the mean size of crystallites were calculated from XRD peaks at $2\theta \approx 43°$ for Cu and $2\theta \approx 62°$ for K. Therefore, the mean size of crystallites of copper and potassium were 0.22 nm and 0.3 nm, respectively. Therefore, it was observed from this finding that dispersed metallic copper and K_2O particles over the surface of alumina support have almost the same crystal size as mean particle size of the catalyst[64]. According to figures 4-5 to 4-7, it was noticed that surface morphology of

the catalyst was rough as all the particles were aggregated and agglomerated each other over the surface of catalyst. Hence, CO_2 and H_2 will be attracted by active metal components of catalyst surface which is due to morphology of the reduced catalyst[65].

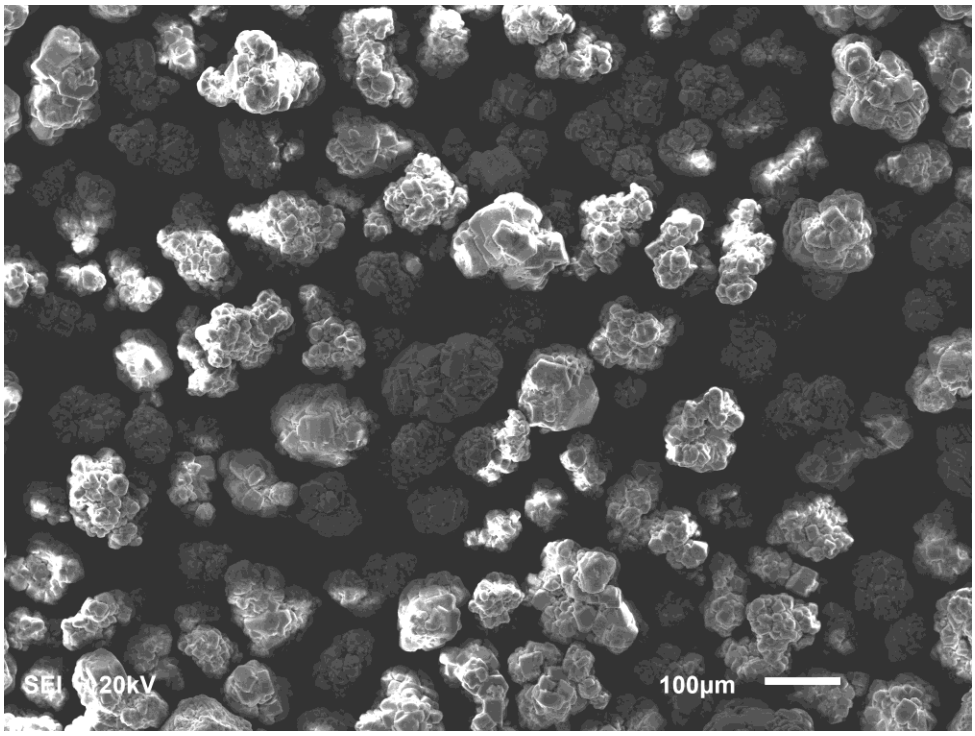

Figure 4-4: SEM image of Al_2O_3 support

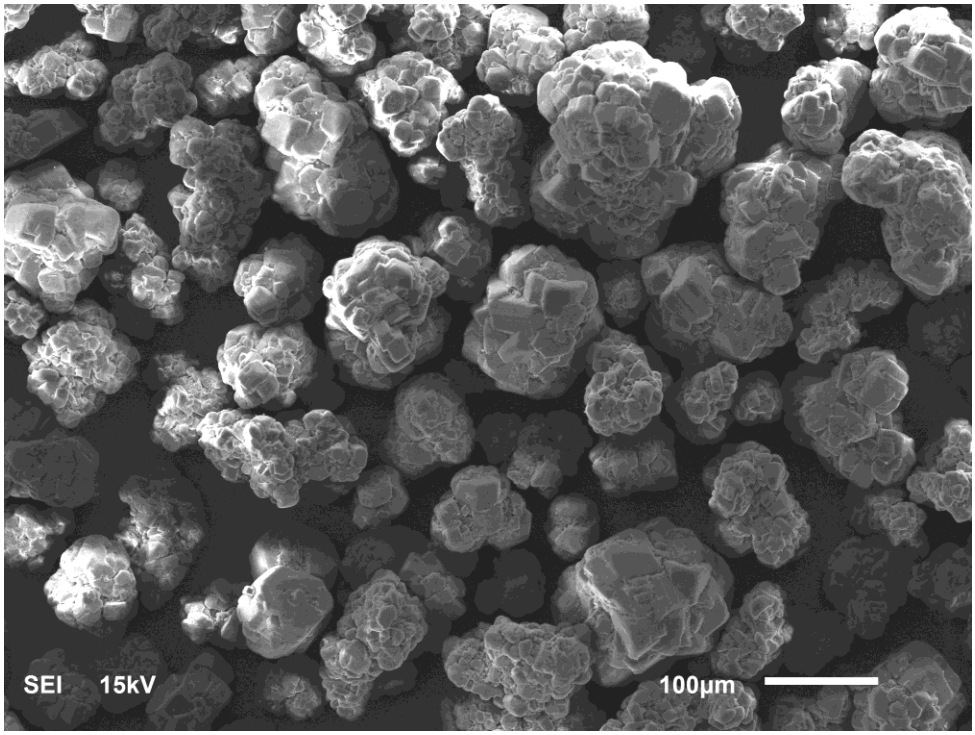

Figure 4-5: SEM image for 1.62%Cu/K(0.5)/ Al_2O_3 catalyst at 100µm resolution

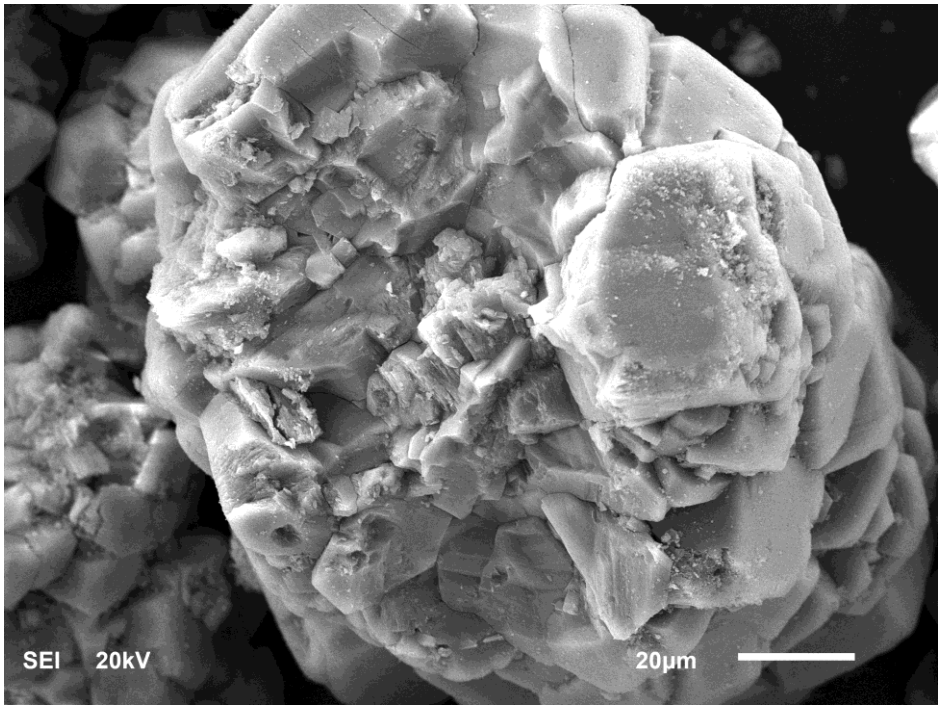

Figure 4-6: SEM image for 1.62%Cu/K(0.5)/ Al_2O_3 catalyst at 20µm resolution

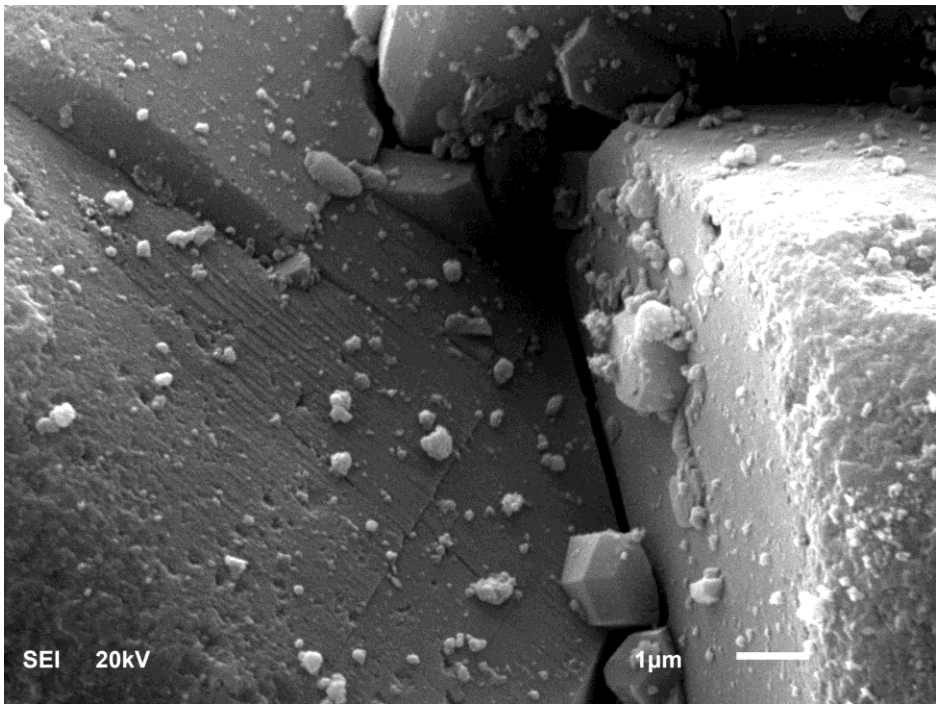

Figure 4-7: SEM image for 1.62%Cu/K(0.5)/ Al_2O_3 catalyst at 1µm resolution

4.1.4 Energy-dispersive X-Ray spectroscopy

Elemental analysis was performed to check the presence of impregnated Cu and K at the surface of Al_2O_3. For this purpose, EDXS technique was used to check the quantity and existence of Cu and K over Al_2O_3 surface. Therefore, EDXS analysis for elemental distribution of selected catalyst particles region was carried out and visualized in the figure 4-8. The image of EDXS for potassium and copper presented a good distribution of both metals over alumina support[66]. According to JEOL certification of ISO 9001 and 14001, the characteristic peaks of Cu are appeared at 8.040 and 0.930 KeV. From figure 4-8, it was noted that indicative peaks of Cu were appeared at same location as mentioned in the energy table for EDXS analysis. Similarly, the peak belonging to K was confirmed at 3.312 KeV from the figure 5. Meanwhile, characteristic peak of Al is observed at 1.486 KeV for region figure 4-8.

Therefore, it is concluded that copper and potassium are impregnated and well distributed over the surface of alumina. Table 4-1 showed the quantity of Cu, K and Al_2O_3 in reduced catalyst. The amount of copper and potassium over alumina support were 1.62% and 0.5% , respectively. On contrary, XRD pattern has also showed the phase of copper, potassium and alumina.

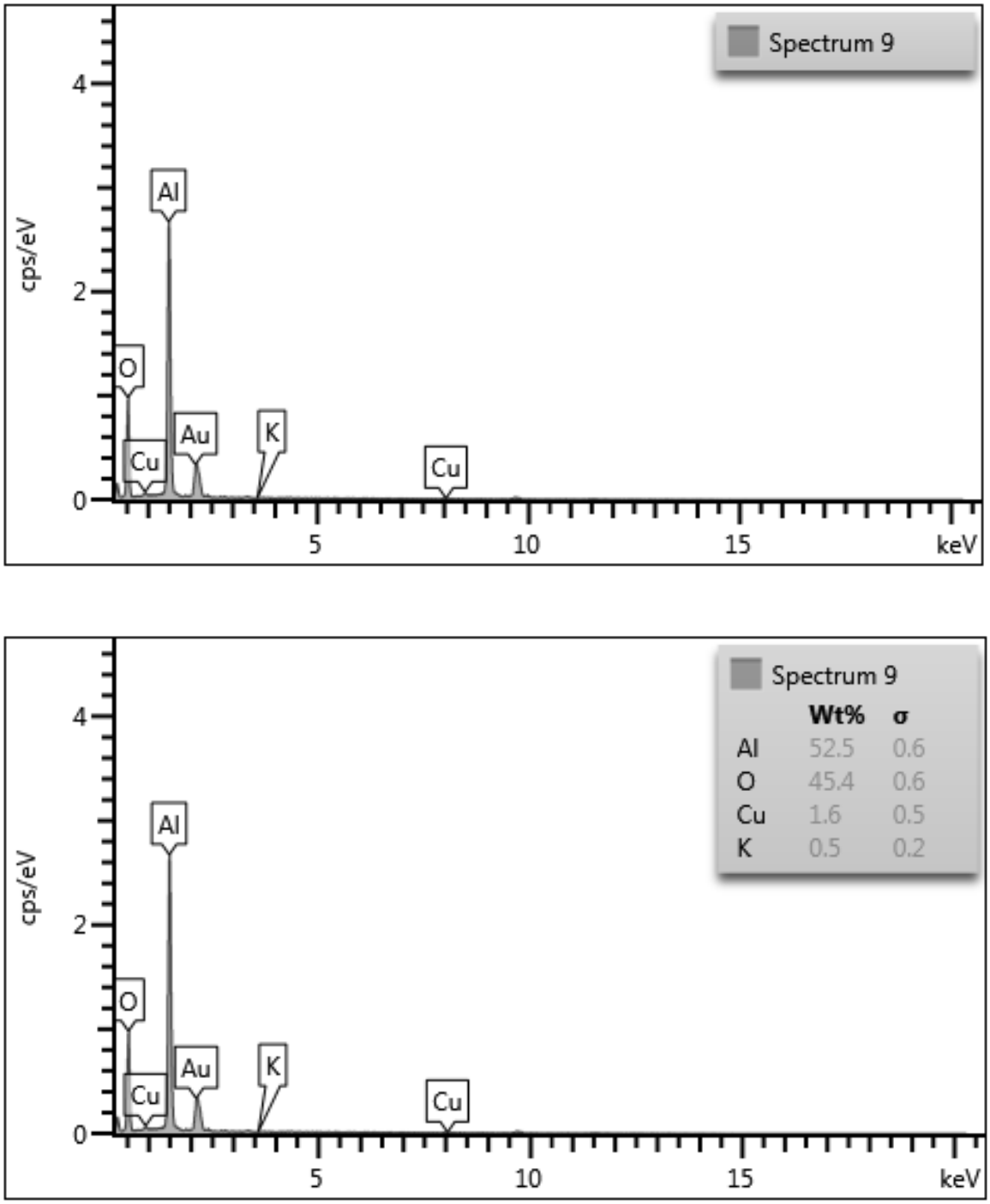

Figure 4-8: EDXS analysis for 1.62%Cu/K(0.5)/ Al_2O_3 reduced catalyst

Table 4-1: EDXS elemental Analysis of 1.62%Cu/K(0.5)/ Al_2O_3 reduced catalyst

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard	Standard Calibration Date
O	K series	12.68	0.04265	45.37	0.64	SiO_2	Yes	
Al	K series	14.86	0.10676	52.52	0.64	Al_2O_3	Yes	
K	K series	0.12	0.00102	0.49	0.18	KBr	Yes	
Cu	L series	0.21	0.00209	1.62	0.50	Cu	Yes	
Total:				100.00				

4.1.5 Brunauer–Emmett–Teller (BET) analysis

Figure 4-9 shows the nitrogen adsorption-desorption isotherms for reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst at 77 K and according to Barrett-Joyner-Halenda (BJH) method, figure 4-10 presents the pore size distribution of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst. Adsorption and desorption values are indicated by the filled and open symbols in adsorption-desorption isotherms, respectively[64]. According to International Union of Pure and Applied Chemistry (IUPAC), the shape of adsorption-desorption isotherm is classified as type IV which is typically a mesoporous material[63,64,67,68]. Meanwhile, a hysteresis loop is formed due to capillary condensation in mesopores which has the shape of H4 type of hysteresis loop[63,68].

It is also noted that the BET surface area and adsorbed volume is reduced by the incorporation of copper and potassium compounds over alumina support which is due to pores obstruction of the active sites in the support[63]. It is also observed that a weak adsorbate-adsorbent interaction is occurred up to 0.45 relative pressure which represents a monolayer-multilayer adsorption because adsorption and desorption follows the same path[64]. The pore size distribution of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst shows the unavailability of pores smaller than 1.7 nm and it is also clear from pore size distribution that few pore which have the pore size greater than 145 nm. Therefore, it is concluded that pore size distribution of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst is arranged between mesopores and macropores as the range of mesopore is the pore between 2-50 nm and range of macropore is the pore greater than 50 nm.

Table 4-2 shows the textural properties of the reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst. According to table 4-2, the BET surface area of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst is 114.98 m^2/g which is calculated from adsorption-desorption isotherm of N_2. Similarly, Barrett-Joyner-Halenda (BJH) desorption cumulative volume of pore and average pore width are 0.255 cm^3/g and 6.21 nm, respectively.

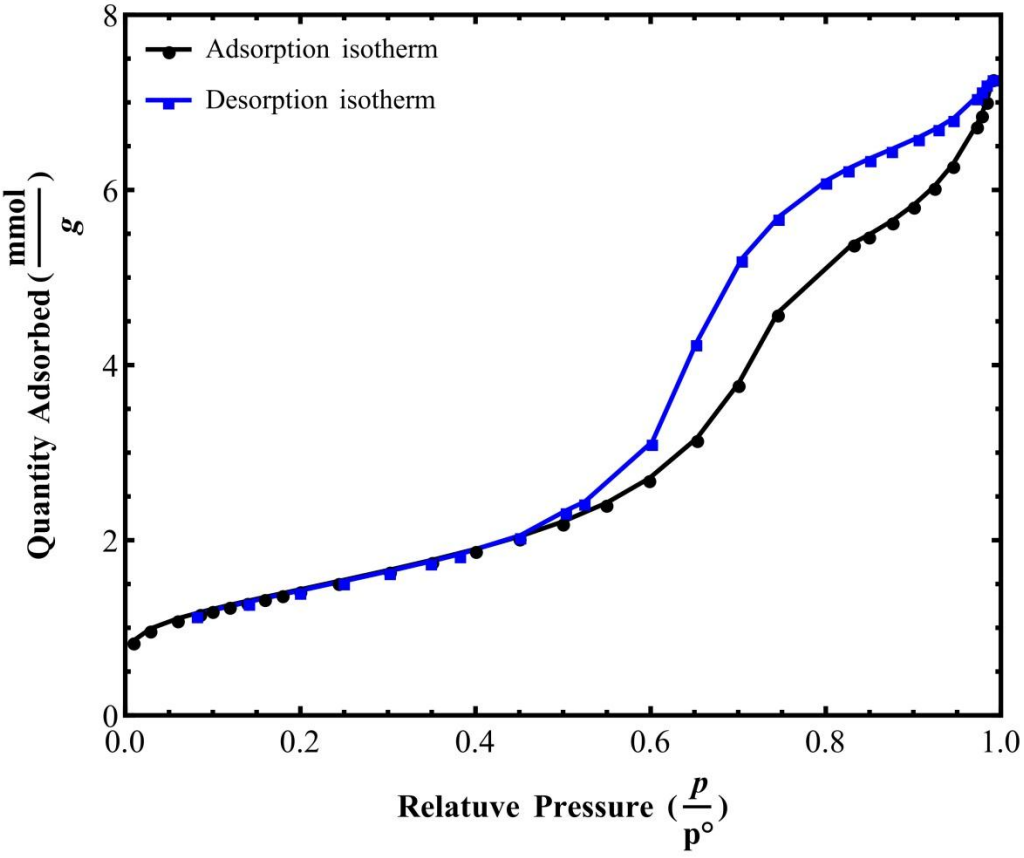

Figure 4-9: N_2 adsorption-desorption isotherm of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst

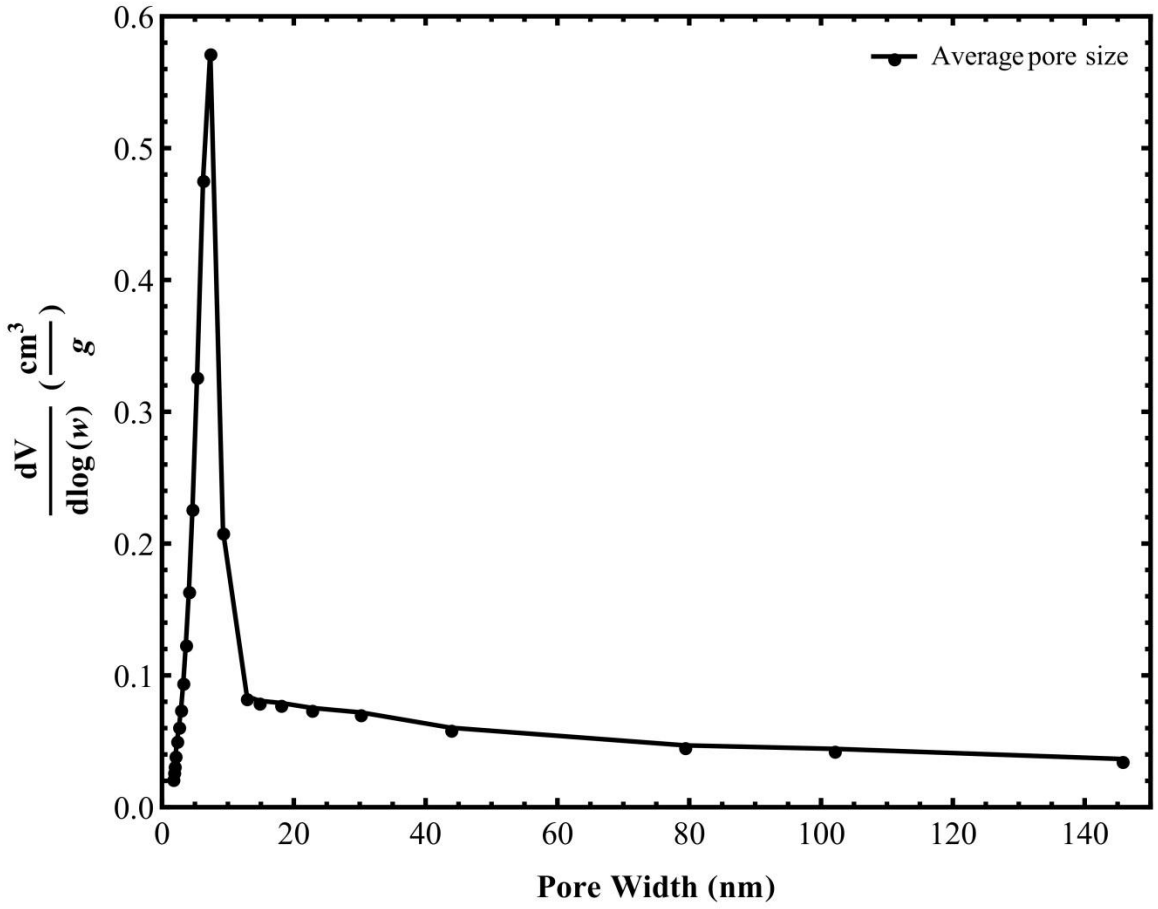

Figure 4-10: Pore size distribution of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst

Table 4-2: Surface area, pore volume and average pore width of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst

Catalyst	Surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]	Average pore width (nm)[c]
1.62%Cu/K(0.5)/ Al_2O_3	114.98	0.255	6.21

[a] BET surface area

[b] BJH desorption cumulative volume of pore

[c] BJH desorption average pore width

4.1.6 Fourier Transform Infrared (FTIR) Spectroscopy

Type of functional group in a catalyst can be investigated by using FTIR analysis. Therefore, it was performed to check the type of functional group and their intensities on the surface reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst. Figure 4-11 shows FTIR analysis of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst which was scanned between the range of 500 cm^{-1} to 4000 cm^{-1} and percentage transmittance was determined. It was also observed that a broad band was appeared between 3000 cm^{-1} and 3700 cm^{-1} for reduced catalyst and minimum value was noticed at 3430 cm^{-1} which was due to stretching vibration of associated and free hydroxyl groups (-OH) on the surface of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst[69].

Similarly, It was checked that the peak appeared at 2360 cm^{-1} was due to the CO_2 which was scanned between 2285 cm^{-1} to 2388 cm^{-1}[70]. Meanwhile, physical adsorbed water was identified by the peak which was appeared at 1640cm^{-1} and it was assigned as bending mode of O-H functional group[57].

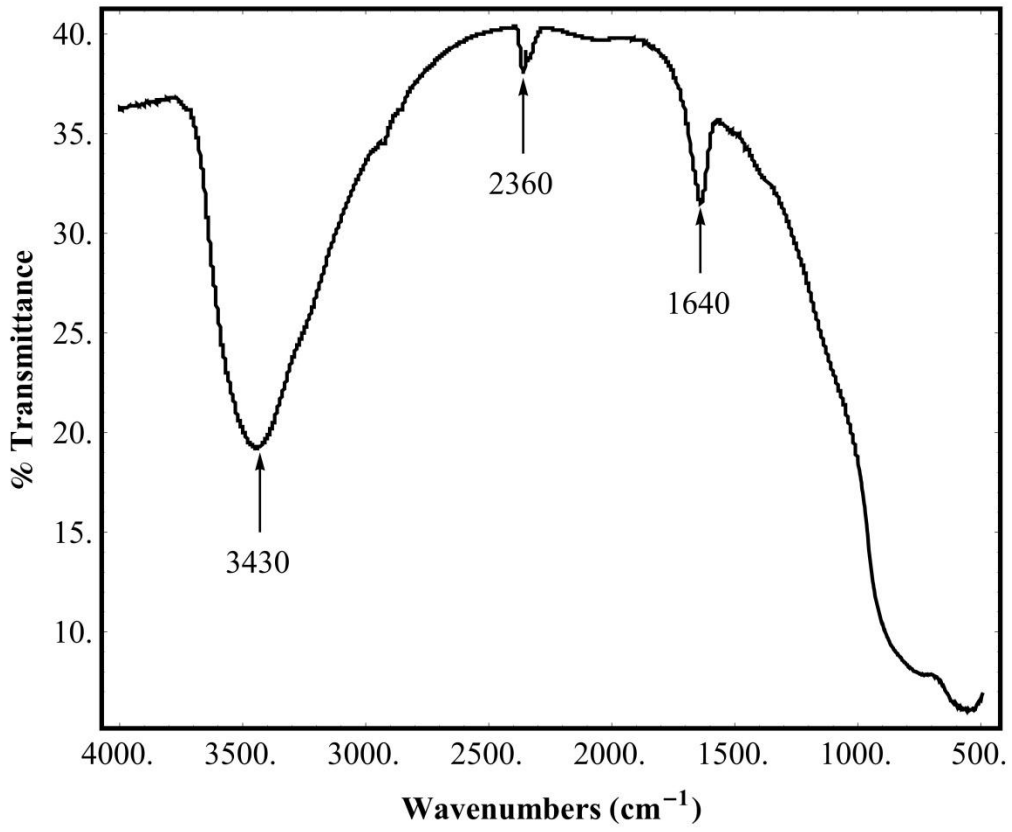

Figure 4-11: FTIR spectrum of reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst

4.2 Catalytic Performance

4.2.1 Performance of catalysts during reaction

Tables 4-3 and 4-4 show the catalytic performance of 1%Cu /Al_2O_3, K(0.5)/ Al_2O_3, 1%Cu/K(0.5)/ Al_2O_3, 1.25%Cu/ K(0.5)/ Al_2O_3, 1.62%Cu/K(0.5)/ Al_2O_3 and 4%Cu/K(0.5)/ Al_2O_3 catalysts for three different temperatures 230 ℃, 400 ℃, and 600 ℃, respectively and two different feed molar ratios of H_2/CO_2 4 and 2, respectively at constant pressure of 7 bar. From tables 4-3 and 4-4, it was perceived that conversion of carbon dioxide was highly dependent on the reaction temperature[71–76]. However, it was noticed that 1.62%Cu/K(0.5)/ Al_2O_3 catalyst has highest conversion of CO_2 for molar ratio of H_2/CO_2=4 at 230 ℃ and 600 ℃ as compared to all other catalysts. 4%Cu/K(0.5)/ Al_2O_3 catalyst has highest conversion at 400 ℃ but the selectivity of methane is very low as compared to all other catalyst.

It was also observed that activity of catalyst was increased by Cu loading till 1.62 wt% copper. It was noticed from tables 4-3 and 4-4 that conversion and selectivity was enhanced by increasing the molar ratio of H_2/CO_2. Therefore, it was concluded that 1.62%Cu/K(0.5)/ Al_2O_3 catalyst showed excellent performance towards carbon dioxide conversion and methane selectivity for feed molar ratio of H_2/CO_2=4 for all temperatures at constant pressure of 7 bar.

Table 4-3: Performance of catalysts during reaction for H_2/CO_2=4

Catalyst	230 ℃			400 ℃			600 ℃		
	X_{CO_2}	S_{CH_4}	S_{CO}	X_{CO_2}	S_{CH_4}	S_{CO}	X_{CO_2}	S_{CH_4}	S_{CO}
	%	%	%	%	%	%	%	%	%
1%Cu /Al_2O_3	1.02	100	0	11.19	48.21	51.79	47.82	26	74
K(0.5)/ Al_2O_3	1.8	100	0	13.89	58.92	41.08	50.83	29.19	70.81
1%Cu/K(0.5)/ Al_2O_3	4.97	100	0	17.2	59.5	40.5	55.23	30.07	69.93
1.25%Cu/K(0.5)/ Al_2O_3	7.51	100	0	25.18	61.18	38.82	59.69	37.9	62.13
1.62%Cu/K(0.5)/ Al_2O_3	11.41	100	0	28.29	66.3	33.7	63.203	39.23	60.78
4%Cu/K(0.5)/ Al_2O_3	10.52	100	0	32.16	32.51	67.49	60.09	11.16	88.84

Reaction conditions for hydrogenation of carbon dioxide: 7 bar and H_2/CO_2=4

Table 4-4: Performance of catalysts during reaction for H_2/CO_2=2

Catalyst	230 ℃			400 ℃			600 ℃		
	X_{CO_2}	S_{CH_4}	S_{CO}	X_{CO_2}	S_{CH_4}	S_{CO}	X_{CO_2}	S_{CH_4}	S_{CO}
	%	%	%	%	%	%	%	%	%
1%Cu/ Al_2O_3	0.1	100	0	9.1	45.55	54.45	34.85	22.18	77.82
K(0.5)/ Al_2O_3	2.3	100	0	6.98	56.37	43.63	41.32	23.47	76.59
1%Cu/K(0.5)/ Al_2O_3	2.99	100	0	9.8	53.26	46.74	43.99	23.59	76.41
1.25%Cu/K(0.5)/ Al_2O_3	6.44	100	0	23.1	62.66	37.34	43.3	34.91	65.1
1.62%Cu/K(0.5)/ Al_2O_3	8.12	100	0	26.93	40.01	59.99	44.08	31.98	68.02
4%Cu/K(0.5)/ Al_2O_3	2.99	100	0	12.26	36.34	63.66	40.28	12.71	87.29

Reaction conditions for hydrogenation of carbon dioxide: 7 bar and H_2/CO_2=2

4.2.2 Effect of Cu loading on catalytic performance of the reaction for $Cu/K/Al_2O_3$ bimetallic catalysts

According to F. Chang et al., surface properties and exposed active sites of catalyst affects the chemical reaction. Therefore, it is necessary for a catalytic reaction to increase the exposed active site. For this purpose, metal loading is increased to enhance the active sites but the dispersion of metal is decreased by increasing the loading[46]. Catalyst does not show good performance during the chemical reaction at poor distribution of metal on the surface of support. Hence, catalyst with optimum metal loading shows better efficiency during a chemical reaction because it has excellent dispersion of metal and has enough exposed active site for reaction.

Cu loading effect was investigated in order to check the optimum loading of Cu for $Cu/K/Al_2O_3$ bimetallic catalysts at which it showed the best carbon dioxide conversion. Figures 4-12 and 4-13 show the effect of Cu loading on conversion of carbon dioxide at three different temperatures and two different molar ratios of H_2/CO_2. It was observed from the figure 4-12 that conversion of CO_2 was increased by increasing the Cu loading up to 1.62 weight percent and then it was decreased at 4% of Cu loading for 230 ℃ and 600 ℃. It is also noticed that carbon dioxide conversion was increased at 4% loading for 400 ℃ but table 4-3 indicated that selectivity of methane was decreased at 400 ℃. Meanwhile, figure 4-13 also shows that conversion of CO_2 was increased up to 1.62% of Cu loading and decreased at 4% copper loading for all three temperatures.

Therefore, it is predicted that decrease in conversion at 4% Cu loading is due to poor distribution of cu metal on the surface of the support because of which methane

selectivity and conversion of carbon dioxide was decreased. Although, increasing the copper loading has enhanced the active site of Cu but dispersion of copper on the surface support was retarded and catalyst performance has been declined due to poor dispersion of Cu metal. According to S. Toemen et al., structure of catalyst pore is blocked due to high amount of metal loading and pore volume and pore size is decreased[77]. Therefore, it can be concluded that amount of Cu loading over alumina support would be optimum to get the good activity of catalyst. The trend of copper loading on the basis of activity has an order of 1.62 wt%> 4wt%> 1.25 wt%> 1wt% for 230 ℃ and 600 ℃. Hence, it can be concluded from figures 4-12 and 4-13 that activity of catalyst is intensely dependent on the catalyst structure, surface composition such as dispersion of metal on the surface of support and 1.62 wt% copper loading with 0.5 wt% K has good activity for hydrogenation of carbon dioxide because it has excellent surface composition and catalyst structure.

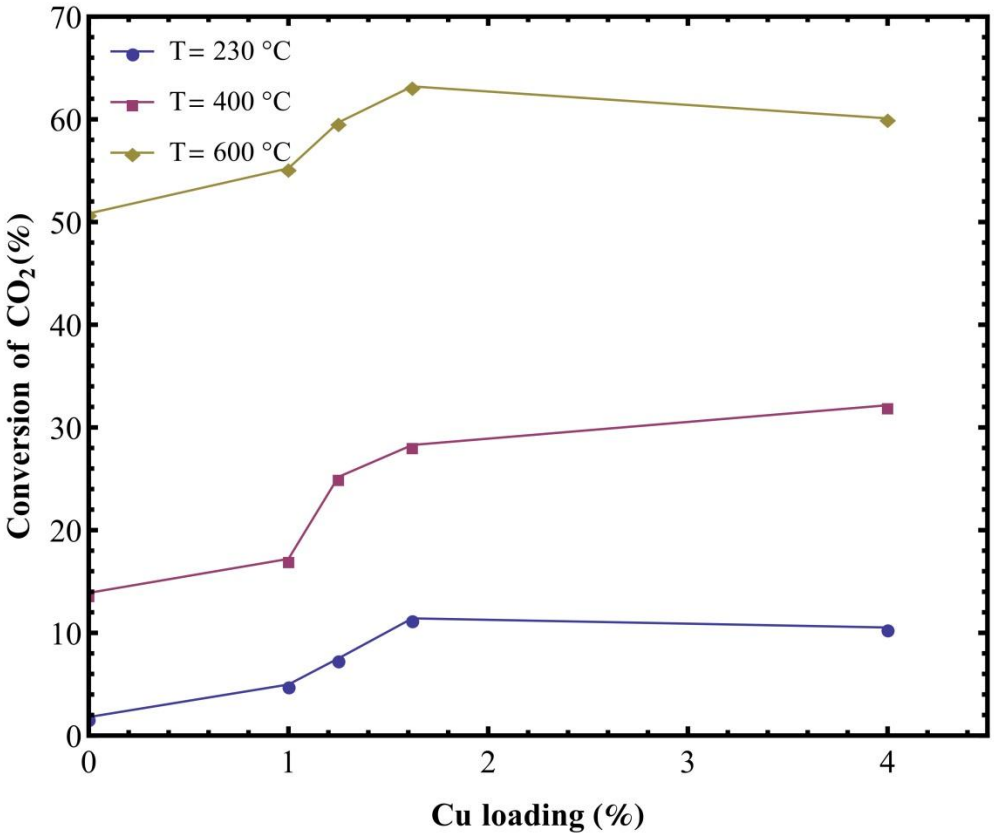

Figure 4-12: Effect of Cu loading on carbon dioxide conversion for H_2/CO_2=4

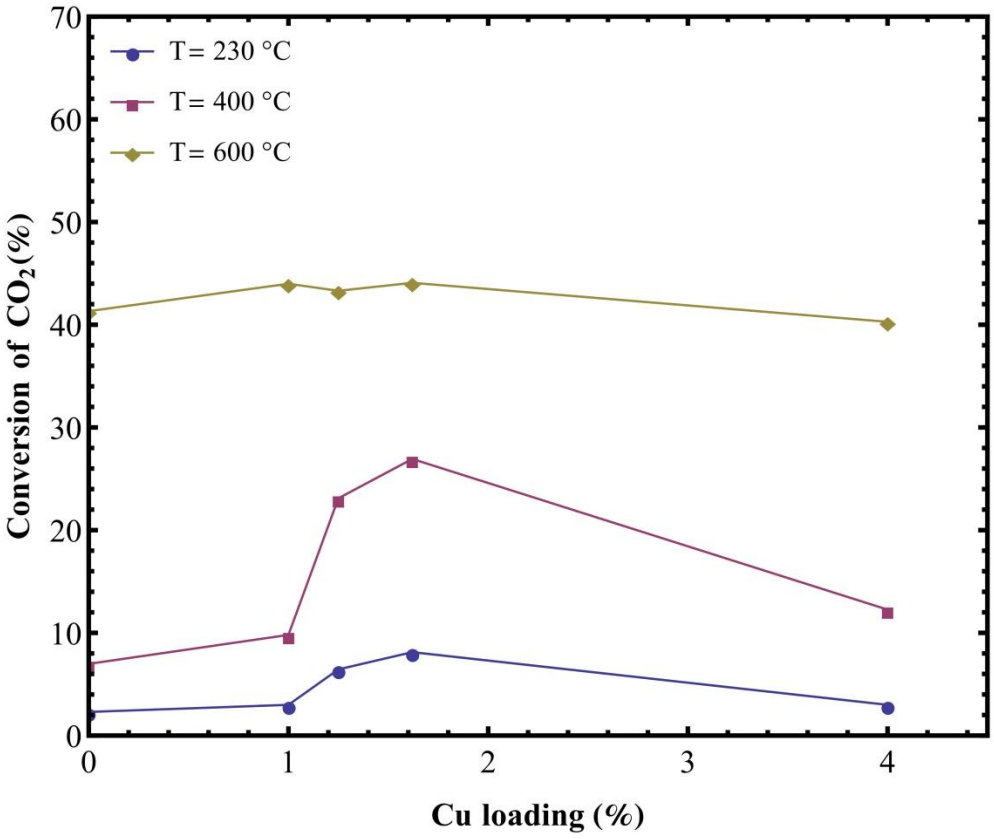

Figure 4-13: Effect of Cu loading on carbon dioxide conversion for H_2/CO_2=2

4.2.3 Effect of reaction temperature on catalytic performance of the reaction

Methanation of carbon dioxide using K(0.5)/ Al_2O_3, 1%Cu/K(0.5)/ Al_2O_3, 1.25%Cu/ K(0.5)/ Al_2O_3 and 1.62%Cu/K(0.5)/ Al_2O_3 catalysts was studied for three different temperatures 230 ℃, 400 ℃, and 600 ℃, respectively and two different feed molar ratios of H_2/CO_2 4 and 2, respectively at constant pressure of 7 bar. Figures 4-14, 4-15 and 4-16 show the effect of temperature on conversion of CO_2, selectivity of CH_4 and selectivity of CO for feed molar ratio of H_2/CO_2=4 at constant pressure 7 bar. Similarly, figures 4-17, 4-18 and 4-19 describe the temperature effect on carbon dioxide conversion, methane selectivity and carbon monoxide selectivity for feed molar ratio of H_2/CO_2=2 at constant pressure 7 bar.

According to figure 4-14, it was observed that conversion of carbon dioxide was increased by raising the temperature and it was reached to maximum value at 600 ℃. All prepared catalysts followed the same trend for temperature effect. For example, at 230 ℃ and molar ratio of H_2/CO_2=4 , conversion of CO_2 for K(0.5)/ Al_2O_3, 1%Cu/K(0.5)/ Al_2O_3, 1.25%Cu/ K(0.5)/ Al_2O_3 and 1.62%Cu/K(0.5)/ Al_2O_3 catalysts was 1.8%, 4.97%, 7.51% and 11.41%, respectively. At 400 ℃, conversion of carbon dioxide for all above catalysts was 13.89%, 17.2%, 25.18% and 28.29%, respectively. Similarly at 600 ℃, it was 50.83%, 55.23%, 59.69% and 63.2%, respectively. Therefore, it is clear from above data that CO_2 conversion was increased by increasing the temperature and 1.62%Cu/K(0.5)/ Al_2O_3 catalyst has good activity for methanation of carbon dioxide as compared to other catalysts. Furthermore, figure 4-17 shows the same trend for conversion of carbon dioxide for H_2/CO_2=2 but it indicates that CO_2 conversion for

K(0.5)/ Al_2O_3, 1%Cu/K(0.5)/ Al_2O_3, 1.25%Cu/ K(0.5)/ Al_2O_3 and 1.62%Cu/K(0.5)/ Al_2O_3 catalysts was low as compared to H_2/CO_2=4.

Figure 4-15 and 4-18 shows the selectivity of methane at different temperatures and it was noticed that selectivity of methane was same for K(0.5)/ Al_2O_3, 1%Cu/K(0.5)/ Al_2O_3, 1.25%Cu/ K(0.5)/ Al_2O_3 and 1.62%Cu/K(0.5)/ Al_2O_3 catalysts at 230 ℃ . On contrary, CH_4 selectivity for all four catalysts was decreased by increasing the temperature as shown in both figures. Correspondingly, figure 4-16 and figure 4-19 shows that selectivity of carbon monoxide was increased by rising the temperature which is due to reverse water gas shift reaction. Therefore, it can be predicted from results that conversion of CO_2 and CO selectivity was enhanced by increasing the reaction temperature whereas CH_4 selectivity was decreased by increasing the reaction temperature which was due to reverse water gas shift reaction competed with carbon dioxide methanation reaction. According to thermodynamic, reverse water gas shift is favored at high temperature and ultimately CO_2 conversion and selectivity of CO was increased whereas selectivity oCH_4 was decreased at high temperature[54,78].

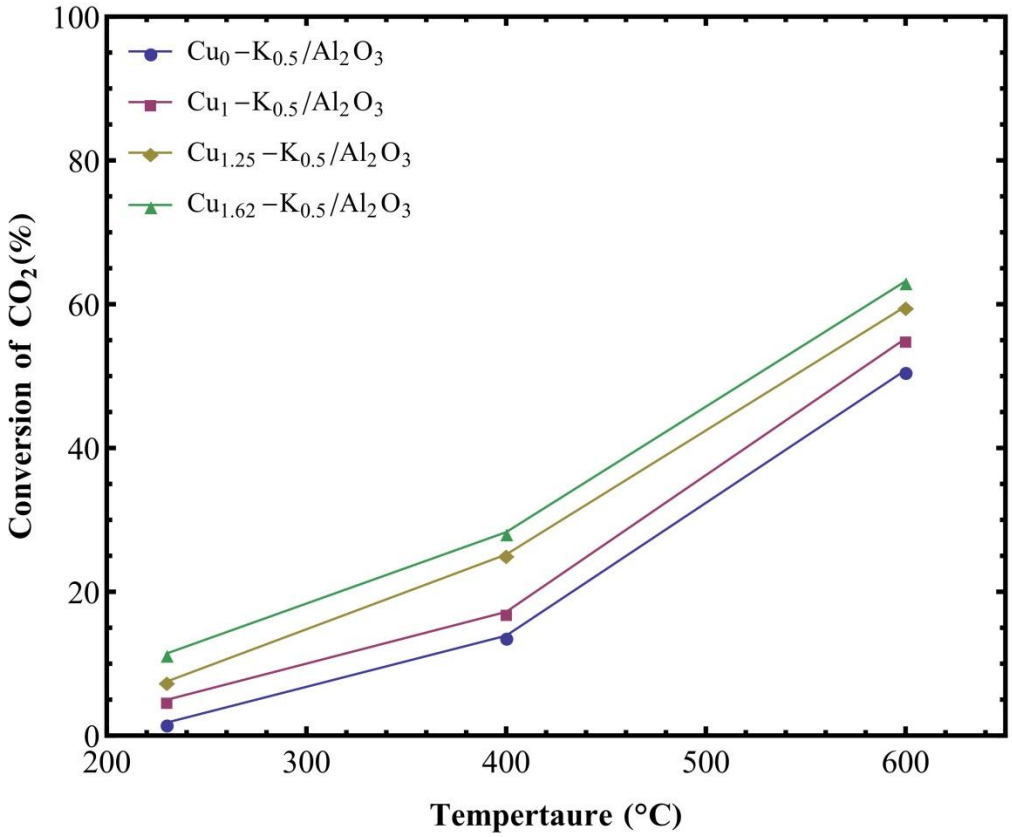

Figure 4-14: Effect of temperature on carbon dioxide conversion for H_2/CO_2=4

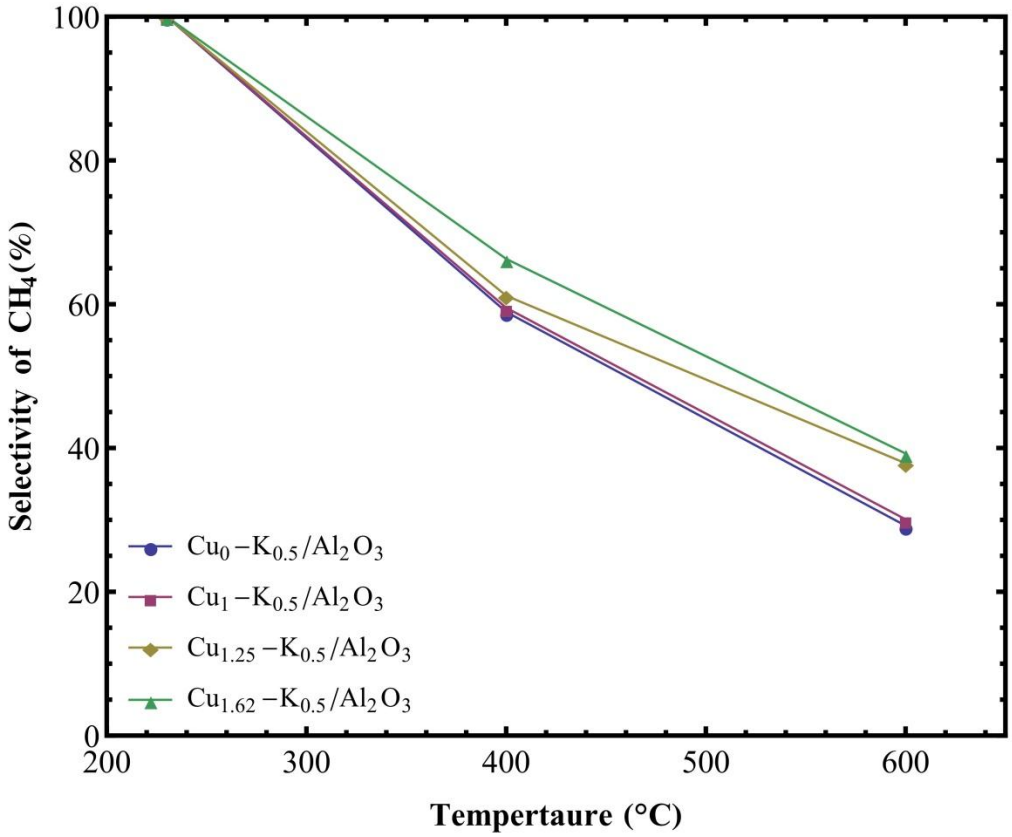

Figure 4-15: Effect of temperature on methane selectivity for H_2/CO_2=4

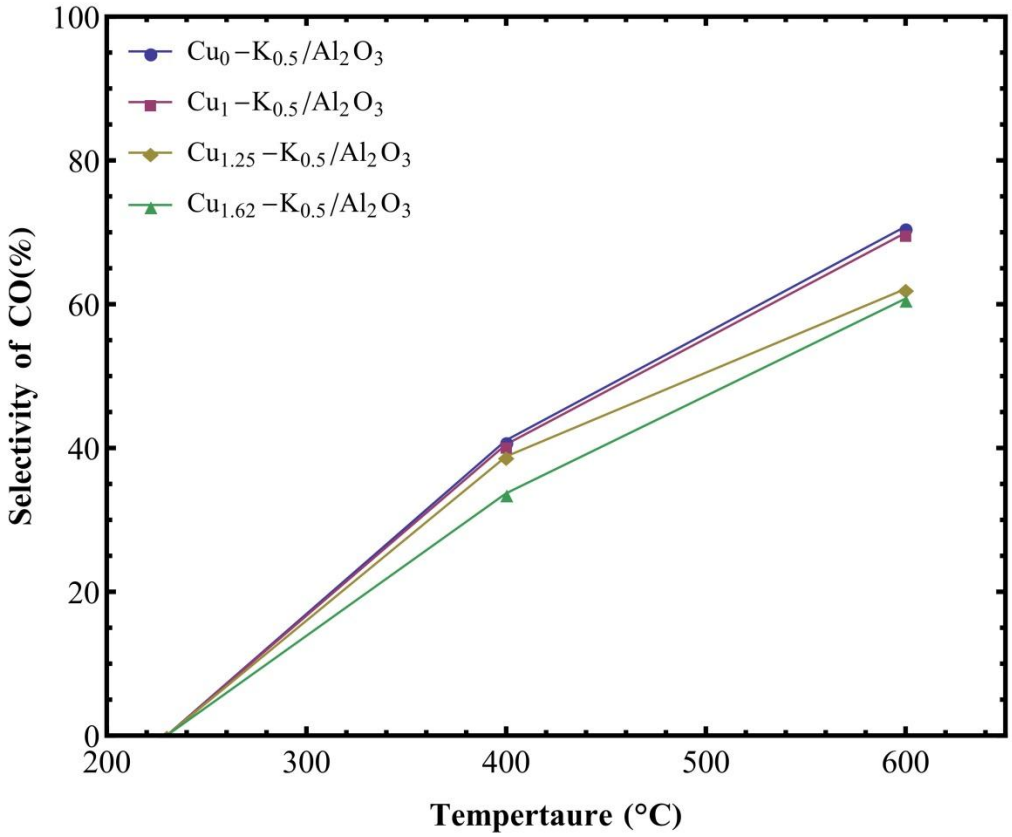

Figure 4-16: Effect of temperature on carbon monoxide selectivity for H_2/CO_2=4

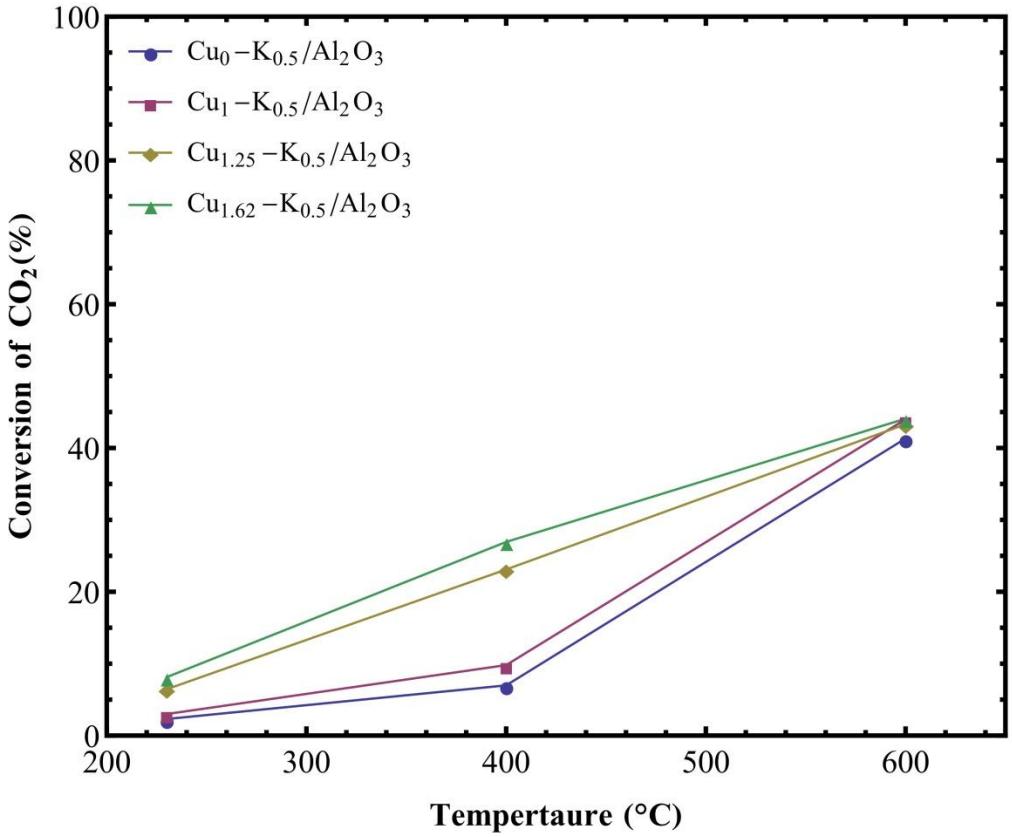

Figure 4-17: Effect of temperature on carbon dioxide conversion for H_2/CO_2=2

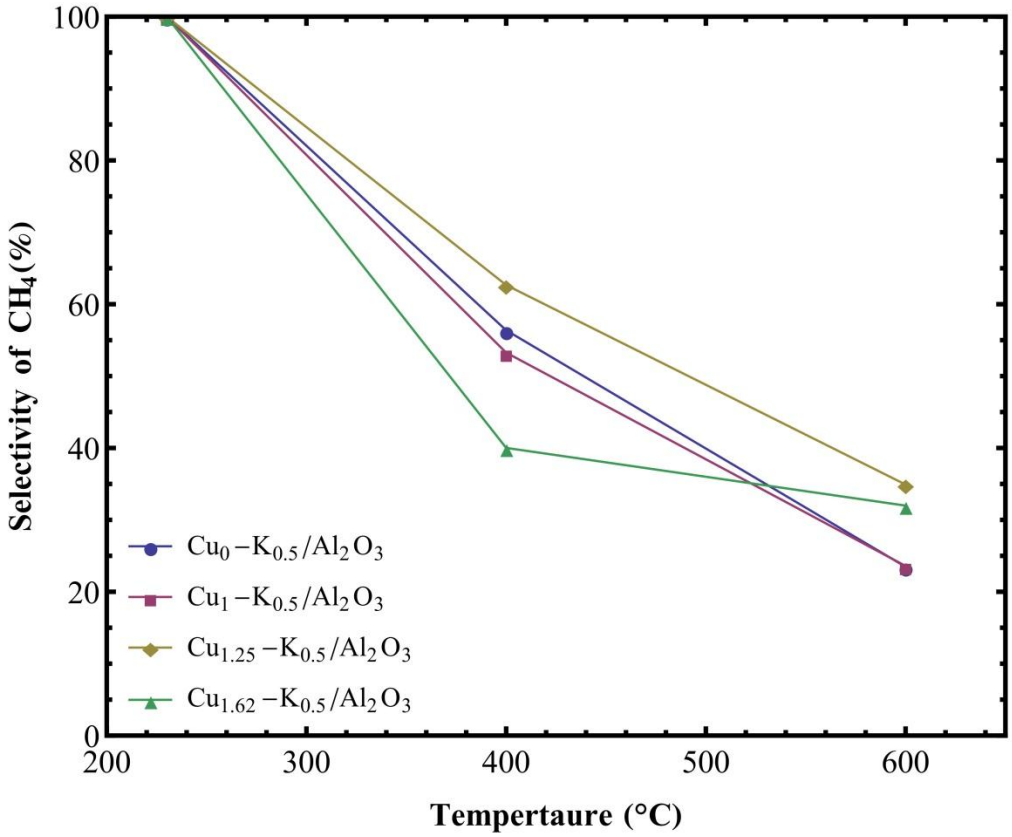

Figure 4-18: Effect of temperature on methane selectivity for H_2/CO_2=2

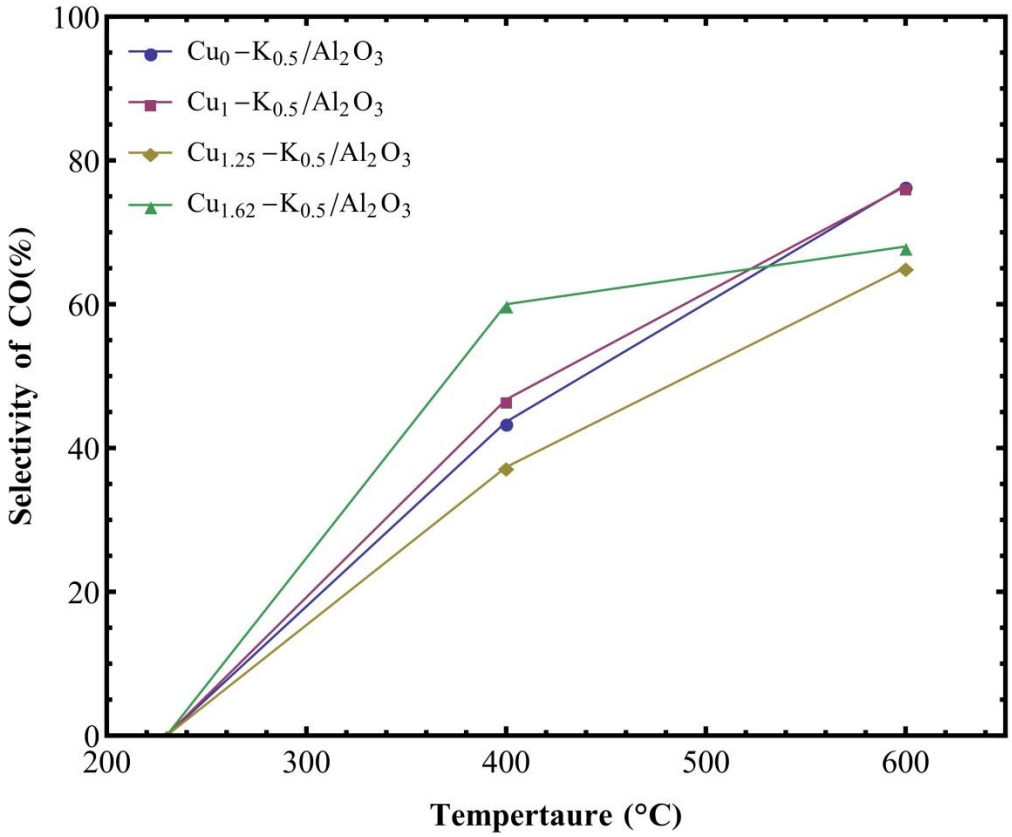

Figure 4-19: Effect of temperature on carbon monoxide selectivity for H_2/CO_2=2

4.2.4 Effect of molar ratio on catalytic performance of the reaction

Figures 4-20, 4-21 and 4-22 show the effect of H_2/CO_2 molar ratio on carbon dioxide conversion, methane selectivity and carbon monoxide selectivity for 1.62%Cu/K(0.5)/ Al_2O_3 catalyst at three different temperatures say 230 ℃, 400 ℃, and 600 ℃. According to experimental results from figure 4-20, it was observed that conversion of CO_2 was incremented by increasing the molar ratio of H_2/CO_2. It is also noticed that when molar ratio is equal to the stoichiometric ratio of Sabatier reaction or methanation reaction, the conversion of carbon dioxide was increased up to 28.29% at 400 ℃ whereas it was 26.93% for H_2/CO_2=2[79].

It was also noticed from figure 4-21 that selectivity of methane was increased by incrementing the molar ratio of H_2/CO_2. Therefore, it is checked that selectivity of CH_4 was 66.3% for H_2/CO_2=4 at 400 ℃. Meanwhile, selectivity of methane was 40.01% for H_2/CO_2=2 at 400 ℃ which showed that the selectivity is also influenced by changing the molar ratio of H_2/CO_2. Similarly, figure 4-22 showed that selectivity of CO was decreased by increasing the molar ratio of the H_2/CO_2. The selectivity of carbon monoxide was 33.7 for H_2/CO_2=4 at 400 ℃. On contrary, it was 59.99 for H_2/CO_2=2 at 400 ℃. Meanwhile, molar ratio of H_2/CO_2 did not affect the selectivity of methane and carbon monoxide at lower temperature say 230 ℃ because at that temperature, there was only methane during the reaction for 1.62%Cu/K(0.5)/ Al_2O_3 catalyst.

Hence, it is concluded that by increasing the molar ratio of H_2/CO_2, conversion of carbon dioxide and selectivity of methane is increased whereas selectivity of carbon monoxide is decreased. Therefore, it is suggested that molar ratio of H_2/CO_2 4 or greater than 4 is

good for the methanation of carbon dioxide because it enhances the conversion of carbon dioxide and selectivity of methane. On the other hand, it suppresses the selectivity of carbon monoxide during hydrogenation of carbon dioxide.

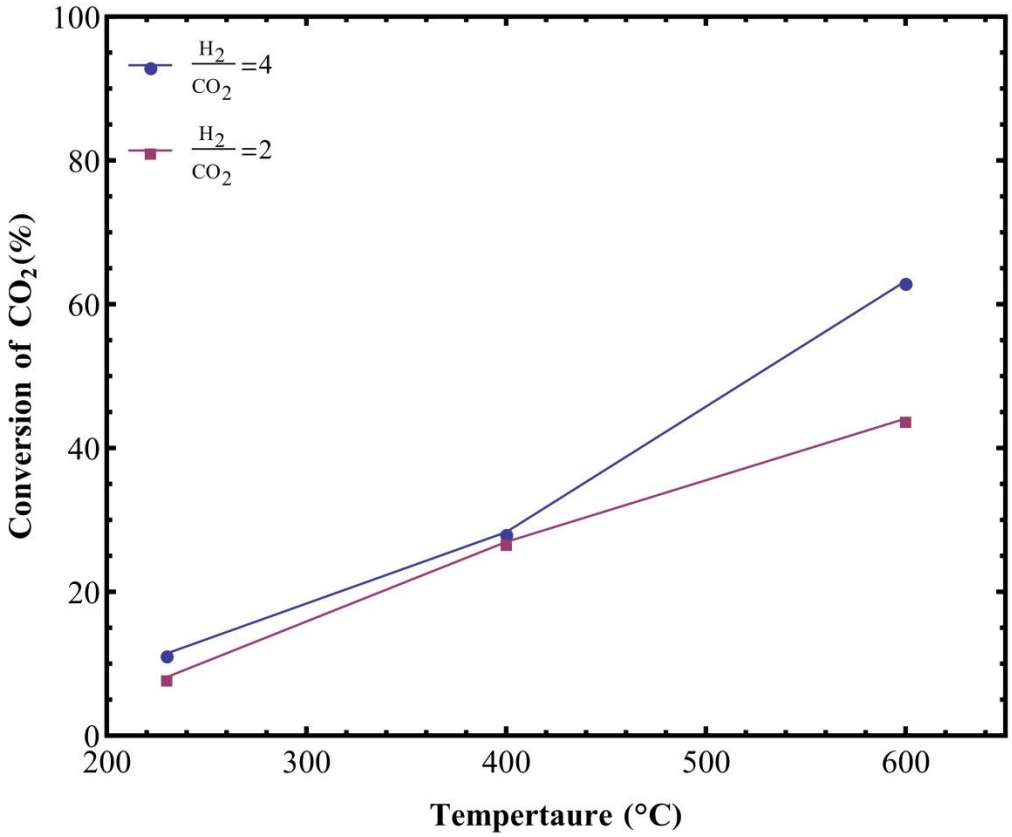

Figure 4-20: Effect of H_2/CO_2 molar ratio on carbon dioxide conversion

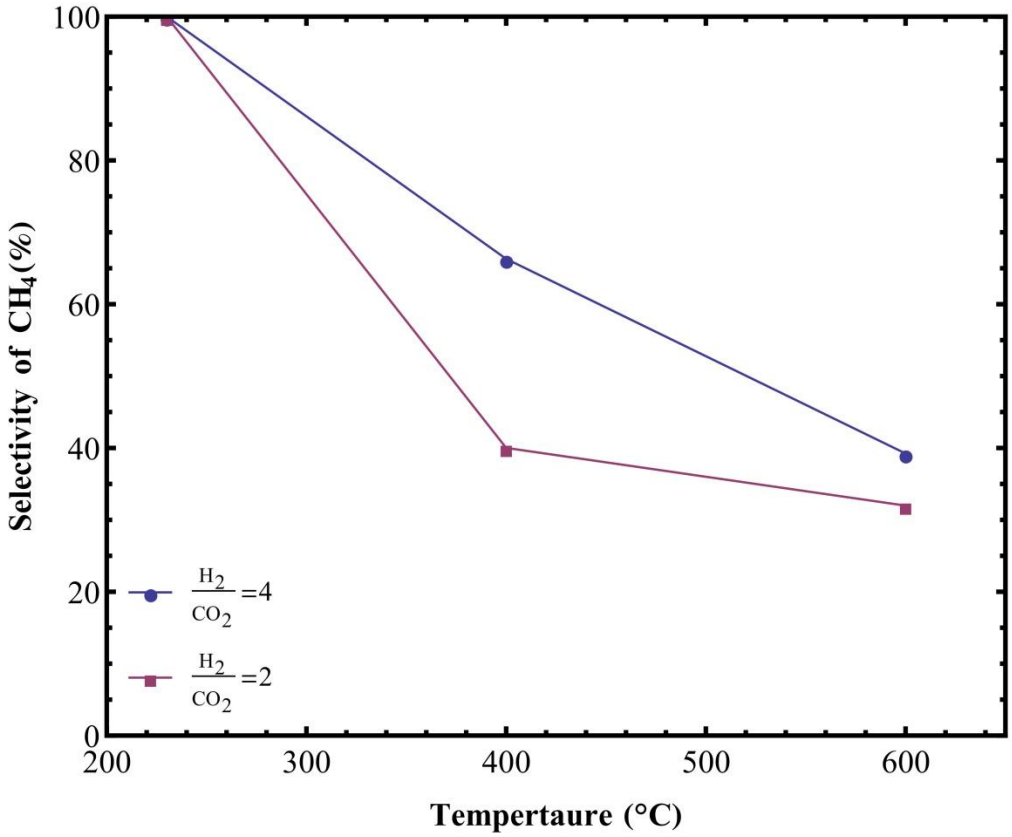

Figure 4-21: Effect of H_2/CO_2 molar ratio on methane selectivity

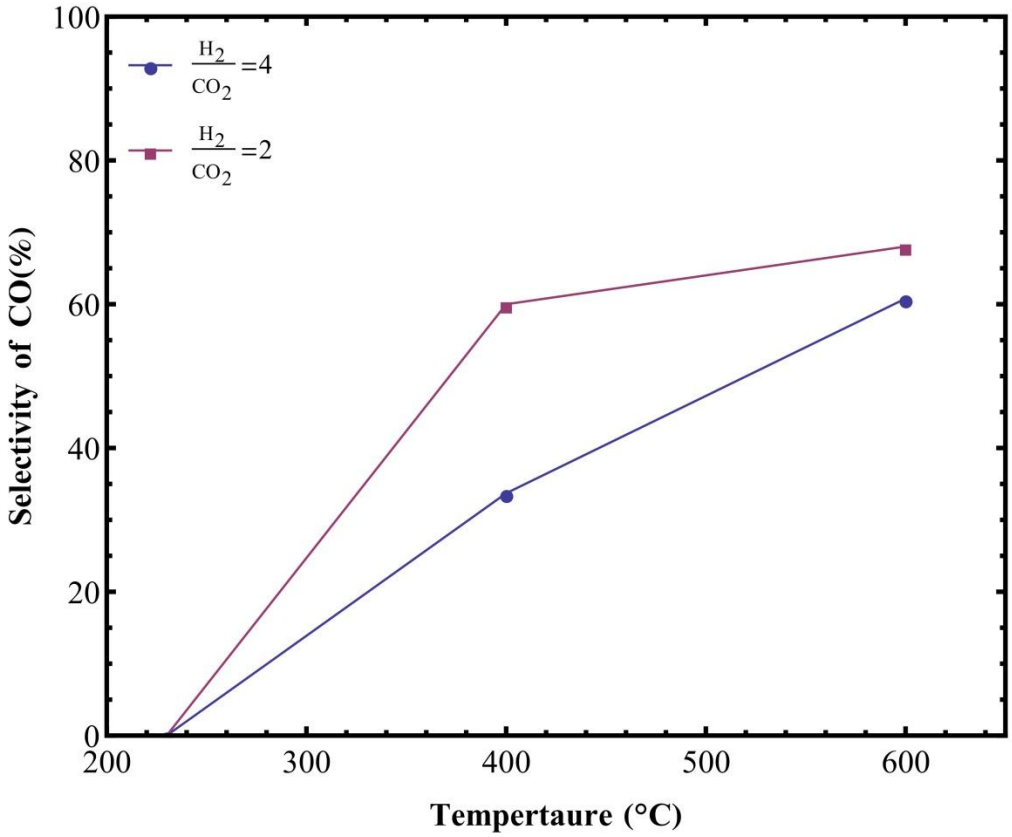

Figure 4-22: Effect of H_2/CO_2 molar ratio on carbon monoxide selectivity

4.2.5 Bimetallic effect on catalytic performance of methanation reaction

Figure 4-23 shows the effect of monometallic and bimetallic catalysts against the conversion of carbon dioxide during Sabatier's reaction. According to figure 4-23, it was observed that conversion of CO_2 for 1%Cu /Al_2O_3 was 11.19% at T=400 ℃, H_2/CO_2=4 & P= 7 bar. On contrary, it was noticed that conversion of carbon dioxide was increased up to 17.2% for same reaction condition when combination of Cu with small amount of K was used. The conversion of carbon dioxide was increased by further increasing the amount of cu up to 1.62% with constant amount of K 0.5 % over alumina support. Figure 4-23 shows that 1.62%Cu/K(0.5)/ Al_2O_3 bimetallic catalyst has 28.29% conversion which is 2.5 times greater than 1%Cu /Al_2O_3 at same reaction conditions.

Therefore, these results reveal that Cu/K/Al_2O_3 bimetallic catalysts enhanced the conversion of CO_2 and selectivity of CH_4 was also increased. Actually, K is acting as a structural promoter during the methanation of carbon dioxide by using 1.62%Cu/K(0.5)/ Al_2O_3 bimetallic catalyst because it was affecting the active sites of the catalyst and dispersion of catalyst over support due to which high conversion of CO_2 and selectivity of methane was achieved[3]. Thus, it can be predicted that K was utilized as a structural promoter for Sabatier's reaction.

Hence, it was concluded that 1.62%Cu/K(0.5)/ Al_2O_3 bimetallic catalyst provided the suitable surface adsorption for H_2 and CO_2 due to which high conversion of carbon dioxide and methane selectivity was achieved[39].The conversions and selectivities for different monometallic and bimetallic catalysts are listed in table 4-3 and 4-4.

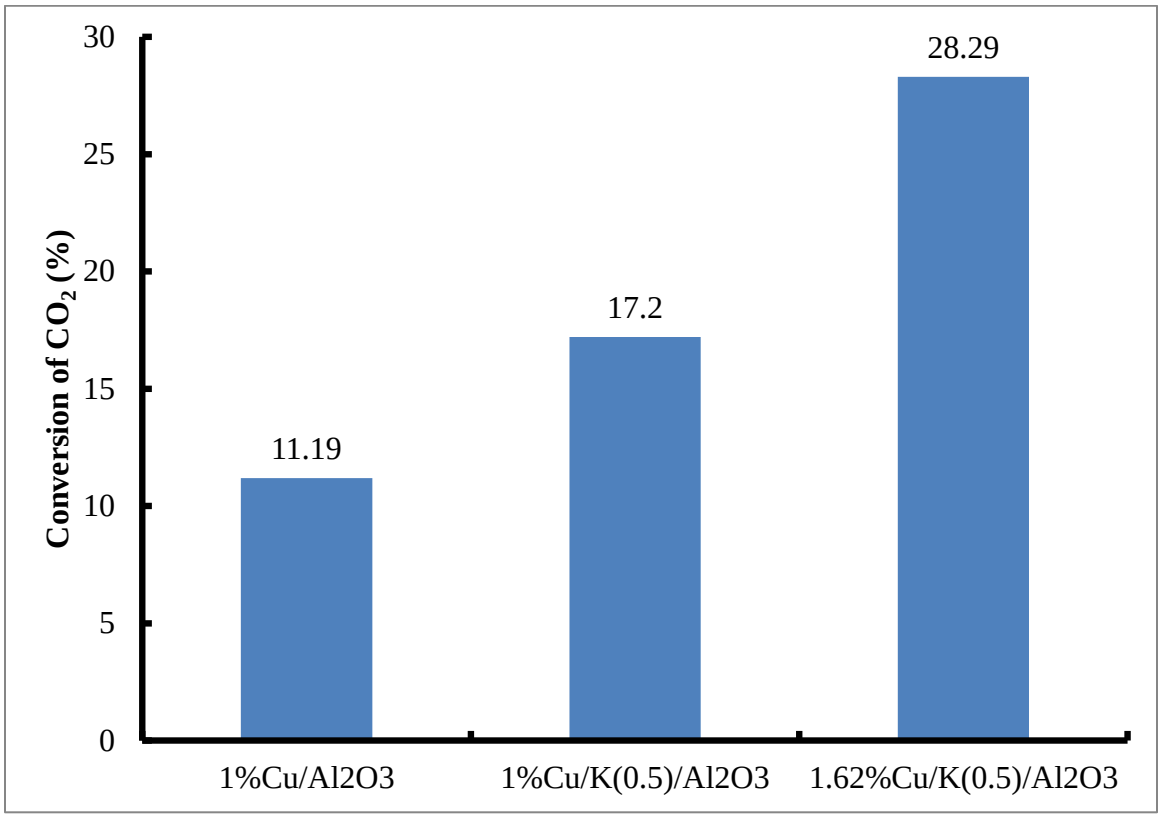

Figure 4-23: Bimetallic effect on catalytic performance of methanation reaction at T=400 ℃, H_2/CO_2=4 & P= 7 bar

4.2.6 Stability and reproducibility activity test

Stability of the reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst was monitored by checking the CO_2 conversion during the methanation reaction of carbon dioxide for 6 h at 230 ℃. Figure 4-24 demonstrates the stability and deactivation of the 1.62%Cu/K(0.5)/ Al_2O_3 catalyst. According to figure 4-24, it was observed that catalyst showed 12 % conversion for first hour during methanation reaction and then it was maintained at 9% conversion for next four hours. After 5 hours, it was noticed that catalyst was started to deactivate. Actually, methanation of carbon dioxide catalysts have a fatal drawback that these catalysts are deactivated due to sintering and metallic phase oxidation due to which metal active sites have been decreased on the surface of catalysts and ultimately influence the stability of catalysts[71].

To check the reproducibility activity of the 1.62%Cu/K(0.5)/ Al_2O_3 catalyst, the in situ reduction of deactivated 1.62%Cu/K(0.5)/ Al_2O_3 catalyst was conducted at 400 ℃ for 4 h. After reduction of deactivated 1.62%Cu/K(0.5)/ Al_2O_3 catalyst, it was again tested for methanation of CO_2 for 6 h with same reaction conditions and figure 4-24 also shows the trend of reactivated catalyst. The activity of the catalyst for first hour was checked by mean of CO_2 conversion and it was noticed that it showed nearly 12% CO_2 conversion. However, it was observed that catalyst was stable at almost 9% conversion of carbon dioxide for next four hours and then it was started to deactivate after 5 h. Interestingly, it was noticed that reactivated catalyst have almost the same trend as compared to fresh reduced 1.62%Cu/K(0.5)/ Al_2O_3 catalyst. Therefore, it can be concluded that prepared catalyst is reproducible but it is stable for only 5 h.

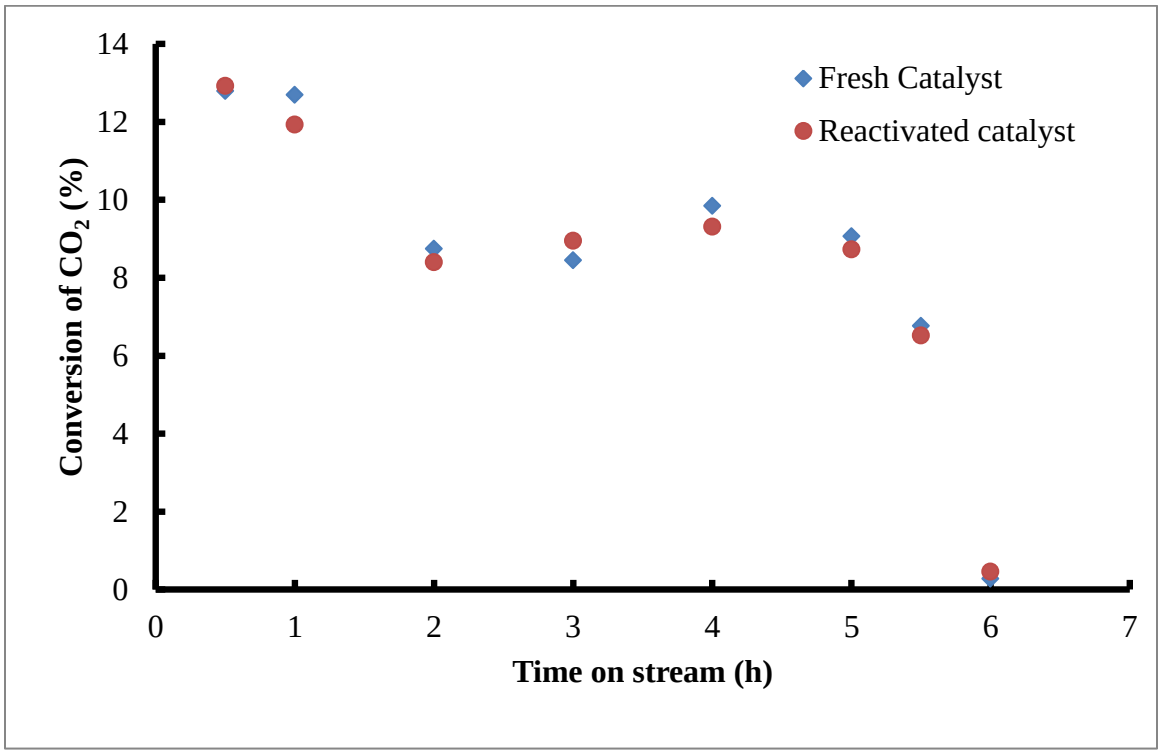

Figure 4-24: Stability and reproducibility activity test for 1.62%Cu/K(0.5)/ Al_2O_3 catalyst at 230 ℃, 7 bar and H_2/CO_2=4 for 6 h

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

For methanation of carbon dioxide, different promoted and non-promoted catalysts were synthesized, characterized and their performance was evaluated on the basis of CO_2 conversion and methane selectivity. On the basis of performance, the conclusion of research for prepared catalysts is given as follow

- XRD analysis confirmed the presence of metallic copper, K_2O over the surface of alumina support.
- TGA analysis of 1.62%Cu/K(0.5)/ Al_2O_3 catalyst after reaction described that observed weight loss is mainly due to deposition of methane and small amount of carbonaceous species on the surface of catalyst.
- SEM analysis showed that surface morphology of 1.62%Cu/K(0.5)/ Al_2O_3 catalyst was rough as all the particles were aggregated and agglomerated with each other. It also described that catalyst has clear edge due to which CO_2 and H_2 will be attracted by active metal components of catalyst surface.
- EDXS confirmed the presence of Cu and K over the surface of alumina support.
- BET analysis demonstrated that 1.62%Cu/K(0.5)/ Al_2O_3 catalyst was mesoporous with a surface area 114.98 m^2/g.

- Cu/KAl_2O_3 bimetallic catalysts provided the suitable surface adsorption for H_2 and CO_2 due to which high conversion of carbon dioxide and methane selectivity was achieved.
- 1.62 wt% copper loading with 0.5 wt% K has good activity for hydrogenation of carbon dioxide because it has excellent surface composition and catalyst structure.
- By increasing the molar ratio of H_2/CO_2, conversion of carbon dioxide and selectivity of methane is increased whereas selectivity of carbon monoxide is decreased.
- 1.62%$Cu/K(0.5)/ Al_2O_3$ catalyst showed good activity at 400 ℃ by giving 28.29% conversion of CO_2 and 66.3% methane selectivity.
- Stability and reproducibility activity test showed that catalyst is stable for 5 h and activity is reproducible.

5.2 Recommendations

Conversion of CO_2 to high value products is like a killing of two birds with one stone in terms of cutting down environmental pollution and giving future energy. $Cu/K/Al_2O_3$ based catalyst shows promising results of CO_2 conversion to methane and carbon monoxide. For the development of effective CO_2 fixation and conversion the current study can be extended by considering the following points for future work.

- Catalyst preparation is the key factor in this research. Proper impregnation of target metal and high porosity is desired during catalyst synthesis step. Although current study encompasses only impregnation technique for synthesis of catalyst but one can test the effect of other catalyst preparation techniques i.e. sol-gel

method, hydrothermal method and incipient wetness impregnation technique using the precursor and metal combinations.

- The effect of impregnation of other metals like Ni, Ce, Co and Zr over the surface of alumina support can also be investigated.
- The support material plays a pertinent role in catalyst synthesis step. Zeolites, Titania and silica based supports can be incorporated for future work.
- The effect of various other operational factors like molar ratio of H_2/CO_2 in the feed stream, the reactor pressure and feed flow rate can also be investigated. Inclusion of these factors will help to design an efficient and economical reactor system.

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JOURNAL PUBLICATIONS

1. Reyad Shawabkeh*[a], Ibnelwaleed Hussein[a], Waqar Ahmad[a], Adeem Rana[a], " Synthesis of a New Cu-Aluminosilicate catalyst for CO_2 capture and conversion to hydrocarbons", Proceedings of the 4th International Gas Processing Symposium, Qatar, October 2014, A volume in Advances in Gas Processing, 2015, Pages 49–58. (Book Chapter)
2. Ali Al-Matar*[a], Waqar Ahmad[a], Adeem Rana[a], Reyad Shawabkeh[a], "Direct methanation of carbon dioxide: Thermodynamic analysis and Performance using $Cu/K/Al_2O_3$ based catalysts" submitted to " International Journal of Hydrogen Energy"
3. Ali Al-Matar[a], Waqar Ahmad[a], Adeem Rana[a], Reyad Shawabkeh*[a], "Characterization and catalytic performance of $Cu/K/Al_2O_3$ based catalysts for methanation of carbon dioxide " (Ready to submit)

4. Waqar Ahmad[a], Ali Al-Matar[a], Adeem Rana[a], Reyad Shawabkeh*[a], "Kinetics study for methanation of carbon dioxide using $Cu/K/Al_2O_3$ based catalysts " (in progress)

CONFERENCE PAPERS

1. Reyad Shawabkeh*[a], Ali Al-Matar[a], Waqar Ahmad[a], Adeem Rana[a], " Synthesis and characterization of new Cu-based catalyst for conversion of CO_2", 7th international workshop characterization of porous material from Angstroms to millimeters, May 3-6, 2015, Florida, USA.